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SOIL SCIENCE

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THE PREFERENTIAL UTILIZATION OF DIFFERENT FORMS OF INORGANIC NITROGEN IN THE DECOMPOSITION OF PLANT MATERIALS

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The experiments described in this paper were carried out with the object of discovering whether the organisms concerned in the decomposition of cellulosic matter exercise any preference for ammoniacal or nitric nitrogen when both forms are available to them in equal concentration.

It is now well established that practically any form of nitrogen will supply the needs of the fungi and bacteria which break down polysaccharide carbohydrates to humus and, in so doing, narrow the wide carbon-nitrogen ratio of the raw material.

Although almost any kind of nitrogen can be used, there are very marked differences in the effects brought about by the process of decomposition. For example, the maximum temperature reached, the color and physical condition of the end product, and the loss of elementary nitrogen sustained are all influenced by the form in which the nitrogen is supplied.

When the carbohydrate is decomposed in the soil it may easily happen that, in addition to the soil nitrate, much nitrogen is also present as ammonia. Such conditions are found when fresh unrotted farmyard manure is ploughed under, or when raw straw is returned to the soil together with a dressing of sulfate of ammonia.

The reactions of soil nitrogen to applications of strawy manure and to raw straw have been studied by many workers, and an extensive literature is devoted to this question. Only a few of these papers will be referred to here.

Niklewski (8) studied the effect of straw on the utilization of nitrogen in various compounds, including ammonium sulfate and sodium nitrate, by an oat crop grown in pots. Only one form of nitrogen was used in each pot, and attention was directed chiefly to effects of concentration and distribution in the soil. This worker, however, noted that straw had an unfavorable influence on the utilization of ammonium sulfate in lower concentrations but that the reverse was the case with similar concentrations of sodium nitrate. In other words, Niklewski found that nitrogen in the form of ammonium sulfate was rapidly immobilized by combination with straw so that the oat crop suffered, whereas sodium nitrate was, apparently, more completely assimilated by the crop in the presence of straw than in its absence. This last observation is rather surprising, but the results are in the same direction as those described in this paper.

Among others, Scott (10), Collison and Conn (2), Murray (6), and Gilbert and Pember (3) have all noted that the application of straw to soil results in a reduction of nitrate with consequent depression of crop yield. This effect could be overcome by addition of sufficient nitrogenous manure. The question of preference for any particular form of nitrogen is not discussed.

EXPERIMENTAL

In the first instance the reactions of ammonia and nitrate with straw were tested alone, unmixed with soil. It is hoped to continue the experiments with nitrogen and straw in both light and heavy soils.

Experiment 1

Air-dried chaffed wheat straw in lots of 20 gm. was well moistened by spraying. Sufficient solution of ammonium nitrate was added to each bottle to supply 1.0 per cent of nitrogen to the straw, half as ammonia and half as nitrate. The additional inorganic nitrogen immobilized as organic nitrogen by 100 gm. of any material in process of decomposition has been termed (9) the "nitrogen factor." As the nitrogen factor of normal wheat straw does not usually exceed 0.8 per cent there would then be a small excess of available nitrogen over and above that immobilized after rotting was complete.

Each bottle contained originally 18.5 gm. of dry matter as straw and 70 cc. water. The bottles were plugged with cotton wool and incubated at 35°C. Since the straw had 0.315 per cent nitrogen in dry matter, the bottles each contained 0.0582 gm. nitrogen in straw and 0.200 gm. nitrogen as ammonium nitrate, or 0.2582 gm. in all.

A bottle was removed at intervals over a period of 160 days for the determination of dry matter and ammoniacal, nitric, and total nitrogen. Ammonia was distilled from a sample made alkaline with magnesia, and nitrate was estimated in the residue by reduction with Devarda's alloy. These methods are known to give high values for both ammonia and nitrate when used on samples containing easily decomposed organic nitrogen. After the thirtieth day, for example, no blue coloration could be found with diphenyl benzidene (5), although the Devarda figure showed 0.04 per cent of nitric nitrogen in the wet sample. The color test is sensitive to one part in a million and it is certain that no nitrate was really present after the thirtieth day. The excess of apparent ammoniacal nitrogen comes, of course, in both cases, from the organic nitrogen and is not originally present as either ammonia or nitrate. More refined methods were used in the second series of experiments with the result that the values for both ammoniacal and nitric nitrogen after 28 days' incubation fell to about one-tenth of those found in the preliminary series.

The figures given in table 1 show clearly that from the start both forms of nitrogen are utilized by the organisms. During the first 15 days, however, when the fungal development is most active, there is a small but definite preference for ammonia over nitrate. On the eighth day, for example, 62 per cent

of the ammoniacal nitrogen but only 33 per cent of the original nitric nitrogen had been removed. In the later stages there is an approximately equal utilization of both forms, but it is very important to remember that the gradual reduction of nitric nitrogen is due to loss as elementary nitrogen as well as to assimilation, whereas the ammoniacal nitrogen is all immobilized if not supplied in excess of the nitrogen factor of the cellulosic base. This difference is more clearly shown in the second series of experiments.

Experiment 2

In this experiment four different sets of bottles, each containing 20 gm. of air-dry oat straw, were incubated for 56 days. Nitrogen was supplied as (*a*) ammonium carbonate, (*b*) ammonium nitrate, (*c*) sodium nitrate and (*d*) a mixture of (*a*) and (*c*). As 0.20 gm. of nitrogen was added to each bottle there was present at the start an excess over the amount expected to be immobilized in rotting. After the 20 bottles of this series had all been analyzed, a final set of five bottles of oat straw was incubated to which 0.32 gm. nitrogen, i.e., more than double the nitrogen factor, was added as ammonium nitrate. The object of this experiment was to determine whether a supply of nitrogen in the form of either ammonia *or* nitrate sufficient to complete the reaction without calling on the other would influence the result.

TABLE 1

Wheat straw rotted with ammonium nitrate at 35°C.

Calculated on 100 gm. of original dry straw

DAYS	LOSS OF DRY MATTER	NITROGEN PRESENT AS			NITROGEN FACTOR
		NH_3	NO_3	Total	
	gm.	*gm.*	*gm.*	*gm.*	*per cent*
0	....	0.54	0.54	1.40	....
1	Nil	0.42	0.55	1.37	0.09
3	3.9	0.44	0.50	1.43	0.18
8	20.4	0.21	0.36	1.26	0.40
15	25.6	0.28	0.31	1.32	0.43
22	29.1	0.23	0.28	1.32	0.52
30	36.2	0.19	.....	1.09	0.56
36	36.0	0.19	0.21*	1.28	0.59
136	56.2	0.13	0.22*	1.14	0.74
160	48.8	0.11	.....	1.17	0.78

* These figures are certainly too high for the reason explained in the text.

Ammoniacal and nitric nitrogen were estimated as follows:

Ammonia. The method was devised by Nichols and Foote (7) for the estimation of free ammonia in sewage and trade wastes. A phosphate buffer solution was made up by dissolving 14.3 gm. KH_2PO_4 and 90.15 gm. of $K_2HPO_4 \cdot 3H_2O$ in distilled water made up to 1 liter. About 10 gm. of the wet manure were

distilled from 300 cc. of water with 25 cc. of the phosphate buffer solution. In this way the separation of the free ammonia from the organic nitrogen was conducted at a pH of about 7.4, which was maintained constant by the phosphate buffer.

Nitrate. This was estimated by Bengtsson's method (1). Ten grams of the wet manure were extracted with 300 cc. of distilled water in fractions of 50 cc. Each fraction was allowed 10 minutes' extraction with occasional stirring. The supernatant solution was decanted through a cotton wool plug filter. This process was repeated until the extract no longer gave a blue coloration with diphenyl benzidene. The suspended organic matter and colloids were precipitated with a few drops of H_2SO_4, and the solution was warmed. The settled matter was filtered off on a Buchner funnel under suction. The filtrate was made alkaline to litmus with NaOH and evaporated down to about 30 cc. After being made up to 200 cc., including 25 cc. of 10 per cent NaOH, the filtrate was again evaporated to 30 cc. By this time any ammonia nitrogen originally present as such and any produced from organic nitrogen in the extract had been volatilized. Usually one evaporation was sufficient. The residue was finally distilled from about 300 cc. of water and Devarda's alloy and the ammonia absorbed in standard acid as usual.

The effect of the improved methods of estimating ammonia and nitrate is clearly seen in table 2. After the fourteenth day of the experiment the amount of ammoniacal nitrogen is about one-tenth of that found in the first experiment (table 1) after an equal period of rotting. The nitric nitrogen is also reduced to a similar extent. Comparison is possible only with the ammonium nitrate series in experiment 2, but the values for inorganic nitrogen are consistently low in the later stages of all the series in which other nitrogen compounds were under test.

The preference of the organisms for ammoniacal nitrogen in the first 14 days shown by the preliminary experiment is confirmed in the two series of experiment 2 in which the nitrogen was supplied as ammonium nitrate and as a mixture of ammonium carbonate and sodium nitrate. Further, if the figures for series (*a*) ammonium carbonate, are compared with series (*c*) sodium nitrate, it will be noticed that on the seventh day the ammoniacal nitrogen has been reduced by 96 per cent but the nitric nitrogen by only 59 per cent. By the fourteenth day the maximum amount of nitrogen had been converted to protein in all three series where nitrate was originally added, after that the nitrogen factor declines and the residual inorganic nitrogen is usually less than 0.10 per cent of the dry matter in the sample. On the other hand when the nitrogen is supplied entirely as ammonia the nitrogen factor remains at a maximum up to the fifty-sixth day, and the percentage of nitrogen in the final product is higher than in any other samples of this experiment. At this stage the ammonification of protein has begun, so that rather more ammonia is found on the fifty-sixth than on the twenty-eighth day, irrespective of whether the nitrogen was originally supplied as ammonia or nitrate.

TABLE 2

Oat straw rotted with different nitrogen compounds at 35°C.

Calculated on 100 gm. of original dry straw

DAYS	DRY MATTER	NITROGEN PRESENT AS			LOSS OF N	NITROGEN FACTOR
		NH_3	NO_3	Total		
	gm.	*gm.*	*gm.*	*gm.*	*per cent*	*per cent*
			(*a*) *Ammonium carbonate*			
0	100.0	1.15	....	1.64	....	....
3	100.0	0.84	....	1.35	17.8	....
7	94.2	0.05	....	1.27	22.7	0.28
14	70.7	0.04	....	1.35	18.0	0.81
28	60.1	0.03	....	1.25	23.9	0.72
56	43.6	0.06	....	1.40	14.8	0.85
			(*b*) *Ammonium nitrate*			
0	100.0	0.57	0.57	1.64	....	....
3	100.0	0.32	0.49	1.27	22.5	....
7	89.1	0.05	0.15	1.21	26.9	0.51
14	65.1	0.03	0.04	1.34	18.6	0.78
28	57.0	0.02	0.01	1.11	32.2	0.59
56	40.4	0.05	0.03	1.15	29.9	0.58
			(*c*) *Sodium nitrate*			
0	100.0	....	1.15	1.64	....	....
3	100.0	0.03	1.01	1.28	22.2	....
7	92.2	0.03	0.47	1.11	32.2	0.11
14	76.3	0.02	0.15	1.14	30.5	0.48
28	62.6	0.02	0.02	1.01	38.4	0.47
56	47.4	0.04	0.02	0.92	44.4	0.36
			(*d*) *Ammonium carbonate and sodium nitrate*			
0	100.0	0.57	0.57	1.64	....	....
3	100.0	0.36	0.48	1.31	19.7	....
7	86.3	0.04	0.12	1.09	33.6	0.44
14	73.9	0.03	0.03	1.31	20.2	0.77
28	62.0	0.02	0.01	1.17	28.7	0.64
56	43.6	0.04	0.02	1.08	34.6	0.52
			(*e*) *Ammonium nitrate (higher concentration)*			
0	100.0	0.93	0.93	2.27	....	....
3	96.1	0.46	0.44	1.32	41.7	....
7	92.7	0.30	0.28	1.32	41.7	0.29
14	73.2	0.06	0.03	1.39	38.8	0.86
28	61.7	0.05	0.04	1.47	35.8	0.94

As the loss of nitrogen during the rotting of the various samples of straw was often considerable and this question is of practical importance, the conditions which gave rise to the greatest loss are worth noting. Throughout the whole experiment, with the exception of the final series with a higher concentration of ammonium nitrate, nitrogen was added in excess of the normal nitrogen factor of the oat straw (0.85) to the extent of 25 per cent. This amount is therefore the greatest loss to be expected if no inorganic nitrogen remained unassimilated. Allowing for the ammonia not volatilized, this result is substantially found in series 2 (*a*) in which ammonium carbonate was used. In the other series, all containing nitrate, there is a greater loss of nitrogen which is at a maximum of 44 per cent in series 2 (*c*) (sodium nitrate). Further, when nitrate is present the nitrogen factor is always lower than when the nitrogen is supplied entirely as ammonia. There seems to be some cause which inhibits the growth of those organisms, probably fungi, responsible for the high proportion of protein found when ammonia is the only source of nitrogen. This effect was most marked in series 2 (*c*) (sodium nitrate). There the nitrogen factor is only a little more than one-half the normal value. The trouble is not due to shortage of mineral nitrogen, for plenty of unused nitrate is present on the fourteenth day when the nitrogen assimilated was at a maximum. Possibly the alkalinity of the rots with $NaNO_3$ (pH 9–10) may be partly responsible, but the effect is noticeable in series 2 (*b*) (ammonium nitrate), where the reaction was approximately neutral. Nitrate does not check the oxidation of the carbohydrates—only the development of protein. Indeed the greatest loss of dry matter in the whole series of experiments, almost 60 per cent, was found in series 2 (*b*) (ammonium nitrate).

Very soon after the first trials of artificial farmyard manure had been made (4) it was recognized that from the economic point of view nitrate was one of the least desirable forms of nitrogen for that purpose. Apart from its high cost per unit of nitrogen the possibility of denitrification must always be present. The experiments described in this paper show clearly how large these losses of nitrogen may be even in bottles where no leaching can occur. Manures made with nitrate nitrogen, in whole or in part, are inferior to those made with ammonium carbonate, as judged by the total nitrogen in the final dry matter and by the nitrogen immobilized per 100 gm. of original straw (nitrogen factor). In the case of sodium nitrate used alone the comparison is particularly unfavorable to nitrate.

Besides richness in protein the yield of manure is also important, and in this respect there is little difference whatever form of nitrogen is used. The loss of dry matter after 28 days is about 40 per cent in all cases. At this stage, equivalent to about four months in a manure heap under average conditions, the products are generally at their best for application to the soil.

When strawy unrotted farmyard manure is applied to a soil containing a reserve of nitrate the organisms have a choice of using either the ammoniacal

nitrogen in the urine-saturated straw or calling on the soil nitrate. These experiments suggest that the ammonia will at first be utilized but that some nitrate will also be built up into protein in spite of the fact that there is more than sufficient ammoniacal nitrogen to satisfy all requirements. At the same time some of the nitrate nitrogen will probably be lost as elementary nitrogen.

A similar series of changes will no doubt occur when raw straw is ploughed into the soil along with sufficient available nitrogen to avoid the depression of crop yield which otherwise follows the immobilization of the soil nitrates. The straw will draw mainly on the ammonia, but some nitrate will also be taken with the usual associated loss of elementary nitrogen.

It is hoped to make some experiments with straw and ammonium-nitrate mixtures in both light and heavy soils to test the validity of the hypotheses submitted.

SUMMARY

When straw is in contact with both ammoniacal and nitric nitrogen in equal initial concentration under conditions favorable for decomposition there is a definite preference by the organisms concerned in the earlier stages of breakdown for ammonia rather than for nitrate.

After 14 days at 35°C. unassimilated inorganic nitrogen is about equally divided between ammonia and nitrate. There is then no apparent preference for either form.

When nitrogen is supplied wholly or partially as nitrate the nitrogen factor calculated after rotting is complete is always lower than when ammonia is used.

The loss of nitrogen is always greatest when nitrate is present. Sodium nitrate and ammonium nitrate lost 30 and 15 per cent more nitrogen, respectively, than ammonium carbonate in equal original concentration.

As a result of this loss of, presumably, elementary nitrogen from nitrate, the relative assimilation of ammonia may be greater than the figures indicate, since the drop in nitrate includes both the nitrogen lost as well as that assimilated.

Some practical applications of these results are discussed.

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RELATIVE AMOUNTS OF CALCIUM CARBONATE AND MAGNESIUM CARBONATE IN SOME MINNESOTA SUBSOILS

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About three-fourths of the improved farm land in Minnesota lies on the Des Moines lobe of the Late Wisconsin drift, or upon outwash or lacustral deposits derived from it. A notable feature of this drift is its calcareousness. In most places on its till plains and clayey moraines carbonates have been leached out to a depth of 2 to 4 feet but below this they constitute from 6 to 30 per cent of the fine earth (5, p. 81; 7, p. 194). Less commonly they are abundant even in the second foot. Fragments of limestone form a large proportion of the gravel and pebbles of the unleached subsoil (4, p. 14).

It is of interest to learn whether the carbonate is present chiefly as calcite or as dolomite in these calcareous subsoils, in which a considerable portion of the roots of some of the most important farm crops develop. The subsoil exposed in drainage ditches provides the most economical source of liming material for nearby lime-deficient soils in some places in northern Minnesota. Analyses showing how the carbonates in the fine earth, the portion passing a 2-mm. sieve, are divided between calcium and magnesium have not been published in this country or in Canada, in so far as we have been able to ascertain.

Soil analyses, as ordinarily made, do not give the desired information, because, although the percentages of lime, magnesia, and carbon dioxide are reported, the lime and magnesia have in part been derived from the decomposition of silicates and from the exchange complex, no matter whether the usual acid extraction methods or those of rock analysis have been used. As a preliminary investigation we have determined the amounts of calcium and magnesium present as carbonates in 25 samples of subsoil of known CO_2 content, selected from collections made in connection with various earlier studies.

SAMPLES ANALYZED

The sets of samples from which the selection was made had been taken to represent various soil profiles, usually to a depth of 6 feet. In most cases the division of the profile had been by arbitrary depths, as second foot, third foot, etc., but in some, according to the soil horizons. Most of the samples represent the uppermost section of the profile that was found to effervesce distinctly when treated with dilute hydrochloric acid. From five of the profiles a sample from a greater depth has been included. All are from sites where the natural drain-

TABLE 1

Relative amounts of calcium carbonate and magnesium carbonate

NUMBER	LOCALITY	SOIL TYPE	DEPTH OF SECTION	MOISTURE EQUIVALENT	CO_2 CONTENT		CARBONATE IN SAMPLE			PROPORTION OF CARBONATES PRESENT AS		RATIO $\frac{CaCO_3 \text{ mols}}{MgCO_3 \text{ mols}}$
					Determined	Computed	$CaCO_3$	$MgCO_3$	Total	Dolomite $CaCO_3$ $MgCO_3$	Calcite $CaCO_3$	
			inches		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
1	Mizpah	Beltrami silt loam	25–36	21.1	4.30	4.09	6.04	2.74	8.78	68.3	31.7	1.87
2	Mizpah	Beltrami silt loam	61–72	18.4	6.85	6.86	10.15	4.60	14.75	68.3	31.7	1.87
3	Taylors Falls	Miami loam	61–72	18.8	3.15	3.51	5.00	2.51	7.51	73.1	26.9	1.68
4	Hamel	Hayden loam	37–48	26.7	4.55	4.86	7.33	3.14	10.47	65.7	34.3	1.98
5	Hamel	Hayden loam	61–72	22.2	7.55	7.65	11.85	4.70	16.55	62.2	37.8	2.13
6	Renville	Webster silty clay loam	25–36	27.3	8.90	8.84	14.81	4.47	19.28	49.7	50.3	2.81
7	Renville	Webster silty clay loam	61–72	26.3	8.65	8.61	13.00	5.56	18.56	65.7	34.3	1.97
8	Canby	Barnes silt loam	25–36	23.3	7.65	7.60	14.29	2.52	16.81	32.8	67.2	4.80
9	Canby	Barnes silt loam	61–72	22.0	7.75	7.75	13.70	3.31	17.01	42.5	57.5	3.50
10	Morristown	Fargo silt loam	13–24	35.6	2.70	3.09	5.54	1.26	6.80	40.5	59.5	3.75
11	Morristown	Fargo silt loam	25–36	35.1	3.70	3.70	5.82	2.18	8.00	59.6	40.4	2.27
12	Albert Lea	Clarion loam	25–36	25.6	2.20	2.29	3.14	1.76	4.90	78.6	21.4	1.51
13	Wells	Webster clay loam	25–36	27.0	5.21	5.21	9.25	2.20	11.45	42.0	58.0	3.57
14	Wells	Webster clay loam	25–36	27.7	6.60	6.09	11.25	2.20	13.45	35.9	64.1	4.34
15	Fairmont	Clarion silt loam	25–36	21.8	7.60	6.97	12.17	3.12	15.29	44.7	55.3	3.30
16	Fairmont	Clarion silt loam	25–36	22.0	7.70	7.69	13.60	3.29	16.89	42.7	57.3	3.49
17	Jackson	Webster silty clay loam	25–36	24.6	6.15	6.07	10.45	2.84	13.29	46.9	53.1	3.10
18	Worthington	Clarion silt loam	25–36	23.7	3.70	3.69	6.50	1.60	8.10	43.4	56.6	3.45
19	Worthington	Clarion silt loam	25–36	26.2	6.50	6.57	11.58	2.84	14.42	43.1	56.9	3.44
20	Adrian	Clarion silt loam	25–36	24.6	4.00	3.66	5.59	2.30	7.89	63.9	36.1	2.05
21	Adrian	Clarion silt loam	25–36	17.0	4.10	3.96	6.45	2.15	8.60	54.7	45.3	2.54
22	Star Island	Cass Lake fine sand	37–72	2.5	0.50	0.46	0.75	0.25	1.00	54.7	45.3	2.54
23	Star Island	Cass Lake fine sand	49–72	2.6	1.80	1.40	2.45	0.61	3.06	43.6	56.4	3.37
24	Star Island	Cass Lake fine sand	61–84	2.5	0.80	0.88	1.55	0.42	1.97	46.6	53.4	3.01
25	Star Island	Cass Lake fine sand	49–72	2.4	1.36	1.34	2.20	0.71	2.91	53.4	46.6	2.62

age was good or moderately so, all were free of chlorides and sodium carbonate, while water-soluble sulfates, including gypsum, were either absent or present only in traces. Pebbles were excluded from all.

The samples were taken by means of augers. Of the 25, 21 are from soil types developed on till plains or clayey moraines, 19 on the Late Wisconsin drift and 2 from Adrian on the Iowan (4, p. 29). All these are composites made from a number of individual samples. In the case of Nos. 1 to 9 each is a composite from 15 sites, 5 sites about 10 yards apart in each of three fields a mile or more apart. Nos. 10 to 21 each represent a single field, Nos. 10 and 11 being taken from 5 sites and Nos. 12 to 21 from 10. The remaining four samples, Nos. 22 to 25, are each from a single boring on Star Island, part of a sandy outwash plain derived from the Late Wisconsin drift (1, p. 282). None are from within the limits of glacial Lake Agassiz (fig. 1).

METHOD OF ANALYSIS

The sample, freed of rock fragments exceeding 2 mm. in diameter, was ground in an iron mortar to pass a 100-mesh sieve. A weighed portion, 5 or 10 gm. according to the richness of the sample in carbonates, was placed in a beaker with 50 to 100 cc. water and treated with the exact volume of 2 *N* HCl corresponding to its CO_2 content. The mixture was stirred frequently, allowed to stand over night, next morning stirred again and transferred to a Büchner funnel. The residue was washed free of chloride, the filtrate was made up to definite volume, and, in an aliquot, calcium and magnesium were determined by the usual methods.

To make sure that the carbonates had been entirely decomposed the residue was treated with hot dilute hydrochloric acid, but in no case was effervescence detected. Very little decomposition of the silicates was caused by the hydrochloric acid. With three samples the amount of SiO_2 in the filtrate was determined and in each found to be less than 0.10 per cent.

In computing the percentages of $CaCO_3$ and $MgCO_3$ it has been assumed that all of the CaO and MgO extracted by this acid treatment were present as carbonates. The amount of CO_2 corresponding to these is reported in the seventh column of table 1 and agrees closely with that actually determined by the use of an absorption tower and titration method. Thus in the case of sample No. 1, in which 4.30 per cent CO_2 was found by absorption, the hydrochloric acid dissolved 3.38 per cent of CaO and 1.31 of MgO, corresponding to 2.66 and 1.43 per cent, respectively, of CO_2, or to a total of 4.09 per cent.

DISCUSSION

As indicated by the moisture equivalents, reported in the fifth column of table 1, all the samples are of fine or moderately fine texture except the four from Star Island. The total carbonate content ranges from 1.00 to 19.28 per cent, and dolomite forms from a fifth to two-thirds of this, assuming that the whole of the magnesium carbonate is present as dolomite, $CaMg(CO_3)_2$.

Accordingly the ratio of $CaCO_3$ molecules to $MgCO_3$ molecules ranges from 1.51 to 4.80, whereas for dolomite the ratio is 1.00. From five localities samples from two depths were analyzed; at two, Mizpah and Hamel, the ratios are similar—1.87 vs 1.87 and 1.98 vs. 2.13, but at the three others the ratios are rather widely divergent, at Renville 2.81 vs. 1.97, at Canby 4.80 vs. 3.50, and

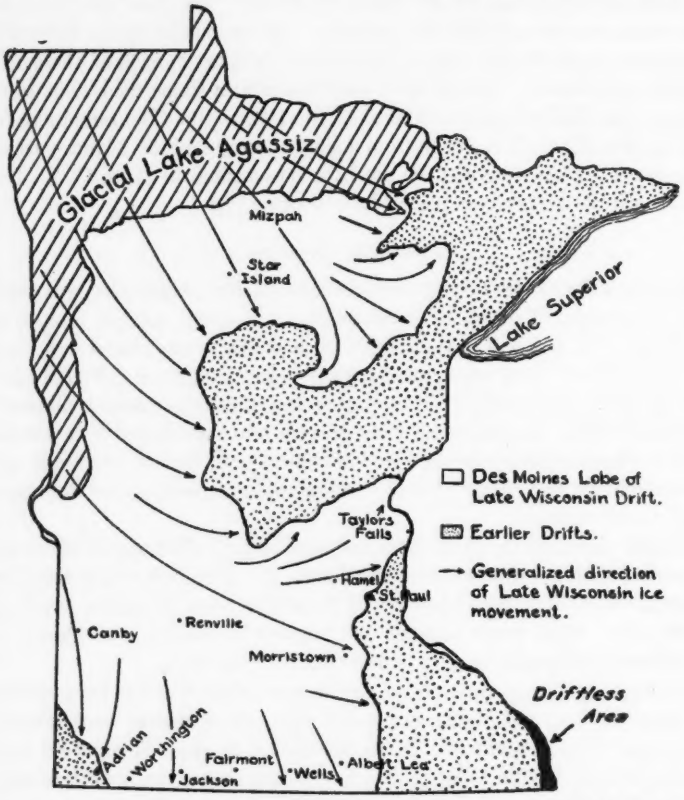

FIG. 1. MAP OF MINNESOTA SHOWING EXTENT IN THE STATE OF THE DES MOINES LOBE OF THE LAST GLACIAL ICE SHEET, DIRECTIONS OF ICE MOVEMENT AND PORTION COVERED BY LAKE AGASSIZ

After Leverett (4, p. 4). The locations of the areas sampled are indicated

at Morristown 3.75 vs. 2.27. Samples from the same depth but from fields a few miles apart show similar ratios at Fairmont, 3.30 vs. 3.49 and at Worthington, 3.44 vs. 3.45, but at Adrian the ratios are more divergent, 2.05 vs. 2.54. At Wells the ratios for samples from the same depth on different parts of the same field are even more dissimilar, 3.57 and 4.34. The four samples from Star Island, taken from sites less than a mile apart, show a range from 2.54 to 3.37.

In no sample does the ratio approach that in dolomite. In the heavy subsoils the supply of magnesium carbonate is very large, considering possible future crop needs of available magnesium, varying from 25 to 100 tons per acre foot.

Western Manitoba was the glacial gathering ground of the carbonates of the Late Wisconsin drift (4, p. 3–4), limestone rocks in Minnesota being confined to the southeastern corner of the state and to a small area in the extreme northwestern corner immediately adjacent to Manitoba (4, p. 14). The calcareous material of this drift was in part brought from Manitoba by the last ice sheet and in part derived from the older, Kansan and Nebraskan, drifts, over which it passed in its southeastward advance (fig. 1), both of which had

TABLE 2

Composition of Manitoba limestones

From reports of Goudge (2, p. 4–8; 3, p. 105) and Wallace and Greer (8, p. 33–52)

NUMBER	LOCALITY	$CaCO_3$	$MgCO_3$	RATIO $\frac{CaCO_3 \text{ mols.}}{MgCO_3 \text{ mols.}}$	NUMBER	LOCALITY	$CaCO_3$	$MgCO_3$	RATIO $\frac{CaCO_3 \text{ mols.}}{MgCO_3 \text{ mols.}}$
		per cent	*per cent*				*per cent*	*per cent*	
1	Sifton Narrows	53.80	45.55	1.00	17	Tyndall	84.46	13.57	5.24
2	Garson	51.08	41.90	1.02	18	Tyndall	85.92	12.34	5.85
3	Stony Mountain	53.79	44.37	1.02	19	Garson	89.67	8.40	8.97
4	Cormorant Lake	53.21	43.26	1.03	20	Oak Point	89.14	7.82	9.57
5	Stonewall	54.82	44.84	1.03	21	Oak Point	90.00	7.19	10.51
6	Stonewall	53.51	42.91	1.05	22	Oak Point	89.08	6.81	10.98
7	Garson	48.11	37.95	1.06	23	Garson	94.02	4.33	18.26
8	Broad Valley	55.35	43.26	1.07	24	Oak Point	95.44	2.78	28.84
9	Broad Valley	55.05	42.75	1.08	25	Winnipegosis	94.80	2.12	37.62
10	Stony Mountain	52.63	40.99	1.08	26	Tyndall	97.09	1.68	48.54
11	Stony Mountain	56.25	42.17	1.12	27	Spearhill	96.56	1.42	57.11
12	Stonewall	57.22	41.12	1.17	28	Spearhill	96.11	1.39	58.02
13	Tyndall	68.98	28.16	2.06	29	Spearhill	96.40	1.24	65.13
14	Garson	71.03	23.35	2.56	30	Oak Point	97.26	0.84	97.26
15	Hecla Island	76.21	16.10	3.97	31	Winnipegosis	98.67	Trace	.....
16	Garson	82.12	16.25	4.24					

had the same gathering ground and were similarly calcareous, limestone forming usually 50 per cent or more of the pebbles in these (4, p. 14). Samples 20 and 21 were taken from the Iowan drift, which is somewhat older than the Late Wisconsin but very much younger than the Kansan and appears to have had the same gathering ground.

In Manitoba there are two large areas of limestone, both of Palæzoic age, one bordering Hudson Bay and the other exposed from Winnipeg northwestward to north of The Pas as a strip about 100 miles wide (2, p. 2). Only the latter has influenced the composition of the Des Moines lobe of the Late Wisconsin drift. It includes the basins of Lakes Winnipegosis and Manitoba and

the western half of Lake Winnepeg; in it three geological periods are represented, Ordovician, Silurian, and Devonian. Although high-calcium limestones have been found in various places, the rocks are prevailingly dolomitic. We have found published analyses of 31 samples of Manitoba limestones and from these have prepared table 2, arranging the data in order of approach to pure dolomite. In 12 of the samples the ratio is below 1.18; in 3, between 2.0 and 4.0; and in 8 it is above 25.0, the magnesium carbonate in these being less than 3.00 per cent. The average ratios for the 25 subsoil samples is 2.84, which is far below that in the high-calcium limestones but much above that in the dolomite samples.

It should be pointed out that the method used in collecting the soil samples, the making of composites from a large number of borings a considerable distance apart, prevents the analyses revealing whether there may exist sharp variations in the ratio from level to level in certain calcareous profiles, such as in the upper part of the zone of carbonate accumulation in pedocals (5, p. 79; 6, p. 18). To answer this question the samples should be taken in short sections from individual profiles, as was done by McMiller in a study of the total carbonate content of some soils in western Minnesota (5).

SUMMARY

The relative amounts of calcium carbonate and magnesium carbonate were determined in 25 calcareous subsoils from different parts of Minnesota, most of them from fine-textured soil types developed upon till plains and clayey moraines of the Late Wisconsin drift. The ratio of $CaCO_3$ molecules to $MgCO_3$ molecules ranged from 1.51 to 4.80, with an average of 2.84. If it is assumed that all the magnesium carbonate is present in the form of dolomite the latter constitutes on the average a little more than half of the total carbonates, the minimum found being 32.8 and the maximum 78.6 per cent. In the heavy subsoils the supply of magnesium carbonate is very high in comparison with crop needs of available magnesium, varying from 25 to 100 tons per acre-foot.

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TOXICITY OF MANGANESE TO TURKISH TOBACCO IN ACID KENTUCKY SOILS[1]

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In studies on frenching of tobacco, for several years Turkish tobacco was grown in the greenhouse on soils from some of the Kentucky soil experiment fields. An abnormal condition developed in the plants on soil from certain plots that had received nothing except manure. This began as a chlorosis in the tips of the leaves, later spread over the leaves and, when severe, produced numerous dead areas and much leaf distortion. This condition evidently was not due directly to H-ion concentration, since field superphosphate treatments more or less prevented it; the pH of the soils was no lower than that of water cultures in which plants were uninjured; and the degree of injury correlated only in a general way with pH of the soils. It seemed probable that the injury was caused by aluminum or manganese—more likely the latter. Jacobson and Swanback (2) reported manganese to cause what appeared to be a similar abnormal condition in tobacco grown on certain acid Connecticut soils. Many Kentucky soils have been found to contain considerable amounts of manganese (3, 11). In a preliminary water culture experiment in 1931, manganese additions produced a condition in Turkish tobacco very similar to that in the plants in the soils.

The work reported in this paper was done to determine the cause of this abnormal growth condition. It included the growing of Turkish tobacco in the greenhouse in soils from the experiment fields and in water cultures; analysis of soil leachates; analysis of the plants grown.

EXPERIMENTAL RESULTS

Growth of Turkish tobacco in the greenhouse in soils from the experiment fields

The soils used, certain information about them, and the plan of the soil culture experiments are shown in table 1. Eighteen hundred grams of air-

[1] Contribution from the soils laboratory, College of Agriculture, University of Kentucky, Lexington, Ky. Condensed from a thesis submitted to the graduate school of the University of Kentucky in partial fulfilment of the requirements for the degree of master of science in agriculture. Published with the permission of the dean of the College of Agriculture.

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dry soil were weighed into one-half-gallon glazed earthenware jars. Glass tubes 1.5 inches in diameter extended from above the soil to the bottom of the jars to facilitate watering and aeration. Distilled water was added from time to time to maintain a moisture content of 25 per cent of the dry soil. Two Turkish tobacco plants were set in each jar on January 3, 1933.

TABLE 1

Soils used, field data, and set-up of soil cultures

SOIL EXPERIMENT FIELD	YEAR ESTABLISHED	DATE SOILS OBTAINED†	PLOT NO.	FIELD TREATMENT* TOTAL POUNDS PER ACRE	SOIL CULTURE JAR NO.	KIND OF SOIL
Berea	1913	Oct. 1923	203	M 20,810	1, 2	Gray silt loam
			302	M 12,000 L 6,000	3, 4	Natural drainage poor
Greenville	1913	Oct. 1923	310	M 12,000	5, 6	Tilsit silt loam
			307	M 12,000 L 14,000 SP 2,400	7, 8	
Mayfield	1913	Oct. 1923	307‡ 507‡	M 24,290 M 20,810	9, 10	Memphis silt loam
		1928	202	M 36,180 L 8,000	11, 12	
		1928	204	M 31,560 SP 2,600	13, 14	
Campbellsville	1919	Aug. 1928	713	M 10,000	15, 16	Silt loam soil derived from limestone and shale
		May 1930	203	M 19,360 L 8,000	17, 18	

* M = manure; L = limestone; SP = superphosphate. (In this paper in referring to plot treatments, the manure treatments will be omitted, since they were made to all plots. Plots receiving manure only will be referred to as check plots.)

† These soils had been brought in for various purposes.

‡ Mixture of equal parts of the soil from the two plots.

Six days after the plants were set chlorosis had developed in the Berea and Greenville check jars, 1, 2, 5, 6. In two more days, it had developed in the Mayfield check jars 9, 10; in the manure-phosphate jars 13, 14; and in the Campbellsville check jars 15, 16. On January 18, chlorosis had continued to develop in plants in the Berea and Greenville check jars (nos. 1, 2, 5, 6) but was less in the other plants. On February 7, the chlorotic condition had practically disappeared from all the plants except those in the Berea and Greenville check jars. Injury was very severe in these plants. The leaves were pitted with

brown, irregular spots and were greatly distorted. At no time was chlorosis present in plants grown on limed soils. (See plates 1, 2, and 3.)

Effect of manganese and aluminum on Turkish tobacco grown in the greenhouse in water cultures

Turkish tobacco plants were grown in three experiments in water cultures to which were added varying amounts respectively, of manganese and aluminum. Pint Mason jars were used. One plant was grown in each jar. The culture solution contained the following salts per liter: 1.00 gm. $Ca(NO_3)_2$, 0.25 gm. K_2SO_4, 0.20 gm. $CaH_4(PO_4)_2$, 0.10 gm. $MgCl_2$, 0.001 gm. H_3BO_3, and 1.0 cc. of a saturated solution of ferric tartrate. The solutions were changed daily to maintain the concentration of the various ions. The roots of the plants were washed with distilled water each time the solutions were changed.

In the first experiment plants were set on March 18, 1933, and allowed to grow in the nutrient solution until March 30. At this time the plants had formed new roots and were making good growth. Manganese and aluminum treatments were then added to duplicate jars. In treatment 1, the pH was maintained at 6.2; in treatment 2, at 4.5.[3] Treatments 3 to 6, inclusive, represented additions of 1, 2, 4, and 6 p.p.m., respectively, of aluminum as $Al_2Cl_6 \cdot 12H_2O$. Treatments 7 to 11, inclusive, represented additions of 4, 6, 8, 10, and 12 p.p.m., respectively, of manganese as $MnCl_2 \cdot 4H_2O$. The pH was maintained at 4.5 in these aluminum and manganese-treated cultures. Phosphorus was omitted from the aluminum cultures to prevent precipitation of aluminum phosphate. To supply phosphorus, these plants were alternated daily between the aluminum-treated culture and a similar culture receiving phosphorus but containing no aluminum, a modification of the method of McLean and Gilbert (6).

The injurious effects of all the aluminum treatments were observable within 3 days. The root tips blackened. Roots no longer lengthened but thickened to twice their normal size. Numerous new roots formed above the level of the culture solution but died upon reaching the solution. New roots also formed in the culture solution, but made only small growth before dying. The toxic effect of aluminum on plant roots has been noted in other crops (6, 10, 12). Top growth was reduced, particularly in size of stem and extent of leaf spread. Late in the experiment a slight tipburn developed in the lower leaves of the plants treated with 4 and 6 p.p.m. of aluminum. At no time did any chlorosis develop in the leaves of these plants or any symptoms appear similar to those in the plants in the unlimed soils.

The manganese-treated plants made normal growth. No injury developed in the tops or the roots within a period of 21 days, when the experiment was discontinued.

In the second experiment the cultures contained 15, 20, 25, 30, 35, 40, 45, 50,

[3] The pH of the nutrient solution as made up was 6.2. pH 4.5 was obtained by the addition of HCl.

and 55 p.p.m. of manganese, respectively. The treatments were not in duplicate. The plants were started in the culture solutions at the same time as those in the first experiment, March 18, 1933. The manganese additions were made on April 15. At this time the plants were 4 to 5 inches high and had good root systems. Chlorosis developed in all the plants within 6 days after treatment and increased in severity with increase in manganese addition. Fifteen p.p.m. of manganese produced only a yellowing in the tips and margins of the leaves. With the larger manganese additions, most of the leaf tissue was affected, and there was considerable development of brown chlorotic areas and leaf distortion. The appearance of the plants was very similar to that of the abnormal plants in the soils. The roots were not affected (roots of the plants grown in the soils were unaffected). Funchess (1) reports that manganese injury is very largely confined to the tops of the plants. From observation the manganese treatments did not reduce plant growth in the 13 days the experiment was continued. Plate 4, figure 1, shows the effect of manganese on the plants in these cultures.[4]

In a third experiment the aluminum and manganese additions were made at the time the plants were set. The aluminum treatments were 0.5, 1.0, and 2.0 p.p.m., respectively, and the manganese treatments 15, 20, and 25 p.p.m.

There was no observable effect from 0.5 p.p.m. of aluminum. The other aluminum treatments affected the plants as in first experiment. The three manganese treatments affected the plants as in the second experiment. Fifteen p.p.m. manganese produced slight chlorosis. The other two treatments produced considerable chlorosis and some brown spots.

Effect on manganese toxicity of phosphorus additions to both soil and water cultures

As stated in the introduction, it had been observed that field phosphate treatments largely prevented the development of the abnormal condition in the plants. The soils producing the chlorotic plants in this study were phosphate deficient. On March 1, 1933, 1 gm. of $Na_3PO_4 \cdot 12H_2O$ was added to each of jars 2 and 6, Berea and Greenville check soils, respectively. The plants in jar 2 averaged 3 inches high; those in jar 6, 2.5 inches high. Growth and recovery soon began. By the end of March the plants in the Greenville soil (jar 6) had almost entirely recovered and the plants in the Berea soil (jar 2) had largely recovered. The phosphate treatments were repeated on April 1.[5]

[4] Since this paper was written barley and red clover plants have been grown by the writer in water cultures containing manganese in concentrations of 5 to 40 p.p.m.

Black spots appeared on the tips of the barley leaves in all cultures 4 days after treatment. These spots later appeared over the entire blade and with the heavier manganese concentration also on the stalk. However, no yellow chlorosis developed.

The red clover plants developed yellow chlorosis on the leaf margins of all the new leaves within 8 days after treatment. Five and 10 p.p.m. of manganese produced only yellow chlorosis; with heavier concentrations, dark necrotic areas appeared on the leaves, later followed by leaf distortion.

[5] The additions may have increased the pH of the soil to some extent. This, however, probably was but a small factor in the reduction of manganese injury.

On April 17 the plants in the Berea soil averaged 15.5 inches high, and those in the Greenville soil, 11.5 inches high. The latter plants were entirely free from chlorosis. The former were still chlorotic but less so than on April 1. Photographs of these plants are shown in plate 5.

A second crop was grown in the jars without additional phosphate treatments. The duplicate jars 1 and 5 (not receiving supplementary phosphate treatments) were included. Only one plant was grown in each jar. The plants in jars 1 and 5 developed chlorosis within 5 days after planting. Later these plants became as distorted and necrotic as those in the first crop. No chlorosis developed in the plant in jar 6. A slight chlorosis developed in the plant in jar 2 some 8 days after setting. This later disappeared.

TABLE 2

Analyses of soil leachates, nitrate determinations, and pH of soils

SOIL FIELD	PLOT NO.	FIELD TREATMENT†	POUNDS OF THE ELEMENT PER 2,000,000 LBS. OF SOIL*						NITRATE NITROGEN		pH OF SOIL	
			Al	Ca	Cl	Fe	Mn	S	Before incubation	After incubation	Before incubation	After incubation
Berea	203	M	2.1	124	402	193	243	220	46.2	60.06	4.70	4.57
Berea	302	ML	None	300	348	Nd	22	200	76.7	112.59	6.63	6.08
Greenville	310	M	1.2	57	159	62	53	115	Trace	10.01	5.38	5.16
Greenville	307	MLSP	None	185	116	115	8	121	13.86	30.03	6.62	7.15
Mayfield	507	M	None	70	99	68	21	68	6.84	21.00	5.25	4.94
Mayfield	202	ML	None	350	113	194	9	194	15.40	112.59	7.02	6.84
Mayfield	204	MSP	None	45	94	27	16	64	17.34	25.74	5.00	4.94
Campbellsville	713	M	None	62	119	34	14	37	13.26	37.53	5.42	5.49
Campbellsville	203	ML	None	213	196	47	11	60	153.90	225.00	6.24	6.48

* No water-soluble phosphate in any of the soils.

† M = manure; L = limestone; SP = superphosphate.

Nd = not determined.

In the third water culture experiment a jar was included to which 15 p.p.m. of manganese was added but the phosphorus omitted. Severe chlorosis developed in the plants in this culture. Only slight chlorosis developed on the tips of the leaves of the plants grown in the culture containing 15 p.p.m. of manganese and the usual phosphorus content. (See plate 4, fig. 2.)

Analyses of Soil Leachates

Portions of the experiment field soils weighing 2,500 gm. were incubated in the greenhouse for 2 weeks at temperatures varying from 65 to 80°F. The water content was maintained at 25 per cent of the dry soil weight. The soils were then air-dried and 2,000-gm. portions of each lot leached with 2,000 cc. of distilled water. The first portions of the leachates were poured back until

clear. The leachates were analyzed[6] for aluminum, manganese, calcium, iron, phosphorus, chlorine, and sulfur. Nitrate and pH were determined in separate samples at the beginning and the end of the incubation period.

Results of the analyses are shown in table 2. Little or no aluminum was present in any leachates. Considerable to large amounts of manganese were present in leachates from the unlimed soils. Liming materially reduced the

TABLE 3

Dry weight and ash, manganese, calcium, and phosphorus content of the plants from the soil culture experiment

Plants set January 3, 1933 and harvested April 17, 1933

SOIL AND PLOT NO.	JAR NO.	FIELD TREATMENT	OVEN-DRY WEIGHT OF PLANTS			PER CENT OF DRY PLANT			
			Tops	Roots	Total	Ash	Mn	Ca	P
			gm.	*gm.*	*gm.*				
Berea, 203	1	M	0.78	0.08	0.86	21.16	0.452	1.8	0.134
	2	M†	7.00	1.70	8.70	19.60	0.344	0.68	0.223
Berea, 302	3	ML	21.20	3.20	24.40	12.11	0.018	2.20	0.049
	4	ML	21.30	3.50	24.80	11.85	0.019	2.60	0.050
Greenville, 310	5	M	0.44	0.07	0.51	24.79	0.516	2.50	0.126
	6	M†	3.40	1.00	4.4	13.53	0.190	1.08	0.367
Greenville, 307	8*	MLSP	9.20	1.70	10.9	11.89	0.0023	3.00	0.064
Mayfield, 307 and 507	9	M	6.10	1.20	7.3	8.80	0.0511	1.55	0.106
	10	M	5.80	1.40	7.2	9.49	0.044	1.43	0.096
Mayfield, 204	13	MSP	8.80	1.70	10.5	9.87	0.0298	1.53	0.1231
	14	MSP	9.20	2.00	11.2	9.65	0.0334	1.43	0.1154
Campbellsville, 713	15	M	3.70	1.00	4.7	14.33	0.0790	2.32	0 0645
	16	M	3.00	0.70	3.7	15.80	0.081	2.43	0.0720
Campbellsville, 203	17	ML	8.30	2.00	10.3	14.86	0.0089	2.40	0.0934

* Jars 7, 11, 12, and 18 are not included in the table of analyses, since they were kept for further studies of the frenching which had developed in them.

† Given supplementary phosphate treatments of two 1-gm. applications of $Na_2PO_4 \cdot 12H_2O$.

soluble manganese content of these soils. Better correlation of the abnormal plant growth condition with soluble manganese than with H-ion concentration

[6] The methods used here and in analyzing the plant materials were: Aluminum, "aluminon" method as described by Winter, Thrum, and Bird (15) and as modified by Pierre, Pohlman, Gordon, and McElvane (8); manganese, periodate method as described by Willard and Greathouse (14); phosphorus, Truog colorimetric method (13); nitrate, phenoldisulfonic acid method; pH, hydrogen electrode method; calcium, McCrudden method (5); iron, chlorine, and sulfur, Methods of Analysis, A. O. A. C. (second edition revised to July 1, 1924).

is shown by the Greenville and Mayfield check soils. Plant injury was considerably greater in the former soil. Soluble manganese content was likewise considerably greater in this soil, but H-ion concentration was somewhat less. The effect of superphosphate treatments on manganese solubility is shown by comparing the Mayfield check and phosphate soils. Soluble manganese was less in the latter.

Analyses of plants

At the close of the soil experiments the plants were harvested and the roots were removed from the soil and washed clean with distilled water. After being

TABLE 4

Dry weight and manganese content of the plants from the second water culture experiment

Plants set March 18, 1933; manganese treatments added April 15, 1933; experiment ended April 28, 1933.

CULTURE SOLUTION			OVEN-DRY WEIGHT OF PLANTS			Mn IN DRY PLANT†
No. Culture	Mn	pH	Tops	Roots	Total	
	p.p.m.		*gm.*	*gm.*	*gm.*	*per cent*
1	15	4.5	2.35	0.52	2.87	0.225
2	20	4.5	1.50	0.30	1.80	0.277
3	25	4.5	1.70	0.40	2.10	0.300
4	30	4.5	1.40	0.40	1.80	0.418
5	35	4.5	2.00	0.40	2.40	0.417
6	40	4.5	2.00	0.40	2.40	0.620
7	45	4.5	2.40	0.70	3.10	0.410
8	50	4.5	1.90	0.40	2.30	0.720
9	55	4.5	1.30	0.25	1.55	1.130
10*	0	6.2	1.70	0.40	2.10	0.000
11*	0	4.5	2.15	0.37	2.52	0.000

* These treatments in duplicate; all others single.

† Slight fusion took place in ashing the plants in cultures 3, 5, 7, 9. Apparently this resulted in some loss of manganese.

oven-dried, the plants were weighed and analyzed for manganese, calcium, and phosphorus. The results are given in table 3. There is a general correlation between extent of plant injury as previously described, percentage of manganese in the plants, and amount of manganese in the soil leachates (table 2).

The question arises as to whether the effect of the lime and phosphate treatments in preventing or decreasing plant injury was entirely due to their action in lowering the solubility of manganese in the soil. No other explanation seems necessary in the case of the lime treatments, but this apparently is not true for the phosphate treatments. Perhaps the addition of phosphate had an additional effect in making manganese inactive within the plant. The high percentage of manganese in the plants grown in the Berea and Greenville check jars which received supplementary phosphate treatments (jars 2 and 6, table 3)

is evidence in this direction. Pierre and Stewart (9) have lately suggested that the effect of phosphate treatments in reducing aluminum injury is in part caused by precipitation of aluminum within the plant.

Results of analyses of plants in the second water culture experiment are given in table 4. The percentage of manganese in the plants increased with increase in manganese in the culture solutions.

TABLE 5

Dry weight and manganese and phosphorus content of the plants from the third water culture experiment

Plants set and treated on April 15, 1933; experiment ended April 28, 1933

CULTURE SOLUTION			OVEN-DRY WEIGHT OF PLANTS			PER CENT OF DRY PLANT	
No. Culture	Mn	pH	Tops	Roots	Total	Mn	P
	p.p.m.		*gm.*	*gm.*	*gm.*		
4	15*	4.5	0.50	0.15	0.65	0.923	0.194
5	15	4.5	0.50	0.20	0.70	0.460	0.700
6	20	4.5	0.59	0.15	0.74	0.371	0.690
7	30	4.5	0.48	1.14	0.62	0.443	0.680

* This culture received no phosphorus.

TABLE 6

*Per cent of manganese and phosphorus in the plants of the second crop of Turkish tobacco grown in the Berea and Greenville soils**

JAR NO.	SOIL AND TREATMENTS	Mn			P		
		Water-soluble	Insoluble in water	Total	Water-soluble	Insoluble in water	Total
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Berea M	0.1100	0.0460	0.1560	None	0.0014	0.0014
2	Berea M plus P†	0.0110	0.0009	0.0119	0.0033	0.0073	0.0106
3	Berea ML	None	Trace	Trace	0.0072	0.0115	0.0187
5	Greenville M	0.0730	0.0203	0.0933	None	0.0049	0.0049
6	Greenville M plus P†	0.0027	0.0068	0.0095	0.0043	0.0082	0.0125

* All percentages calculated on the green weight of plant.

† Phosphorus treatments in jars 2 and 6 added as a supplementary treatment for the first crop.

Results of analyses of plants in the third water culture experiment are given in table 5. There was a large increase in percentage of manganese in the plants grown in the culture where phosphorus was omitted as compared with the corresponding culture containing phosphorus. Increase in manganese concentration in the culture solutions also failed to bring about increase in percentage of manganese in the plants. In both these respects the results are not in line with those previously given. It is to be considered that in this experiment the plants were started directly in the culture solutions containing the special treatment and grew only a relatively short time.

Kelly (4) reports work showing a considerable variation in the degree of solubility of the plant manganese in different plants. To obtain information on this point for Turkish tobacco, the plants in the second crop in the Berea and Greenville jars 1, 2, 3, 5, and 6 were harvested (50 days after the plants were set). The stem and leaves were ground with a little distilled water in a mortar until thoroughly macerated and then leached with distilled water. The leachate was analyzed for manganese. The residue was ashed and also analyzed for manganese. The results are shown in table 6. Excepting the plant from jar 6, containing only a low total percentage, most of the manganese was soluble.

SUMMARY AND CONCLUSIONS

Studies were made to determine the cause of a chlorosis in Turkish tobacco grown in soils from unlimed plots of several of the Kentucky outlying soil experiment fields. Previous work here and elsewhere suggested that it was manganese.

Plants were grown in the greenhouse in soils from check and from limed and phosphated plots from the Berea, Greenville, Mayfield, and Campbellsville soil experiment fields, and the extent of injury which developed was noted. Severe to slight injury developed in plants in all the unlimed soils. No injury developed in limed soils. Phosphate treatments very much reduced the injury.

Plants were grown in water cultures containing varying amounts of alunum and manganese. Aluminum additions injured the roots, but there was no effect similar to that in the plants grown in the soils. Manganese in concentrations of 15 p.p.m. in the culture solution used, produced chlorosis in the plants. This became more severe with higher manganese concentrations. The condition of the plants appeared to be the same as that of the plants grown in the soils. Removal of phosphorus from the culture solution lowered the manganese concentration at which injury took place. Cultures were also included to determine the effect of variations in pH. A pH as low as that of any of the check soils had no injurious effect on plant growth.

Additional portions of the soils used in the soil-plant experiments were incubated in the greenhouse for 2 weeks then treated with distilled water and the leachates analyzed for manganese, aluminum, and other constituents. Very little or nor aluminum was found in the leachates. Considerable to much manganese was found in leachates from the soils of the check plots. Liming very largely reduced manganese solubility.

Analyses were made of plants grown in the soils. There was general correlation between extent of plant injury, percentage of manganese in the plants, and amount of manganese in the leachates.

Analyses of plants grown in water cultures with manganese concentrations from 15 p.p.m. to 55 p.p.m. showed the percentage of manganese in the plants to increase from 0.225 to 1.13.

It was concluded that the abnormal growth conditions developing in Turkish tobacco grown in soils from the check plots of outlying Kentucky soil fields is due entirely to soluble manganese. There was some evidence that part of the effect of the phosphate treatment in reducing plant injury was through making manganese inactive in the plant. The findings of this experiment suggest that soluble manganese may be an important factor in the unfavorable effects on crop growth of the acid condition of many soils in Kentucky.

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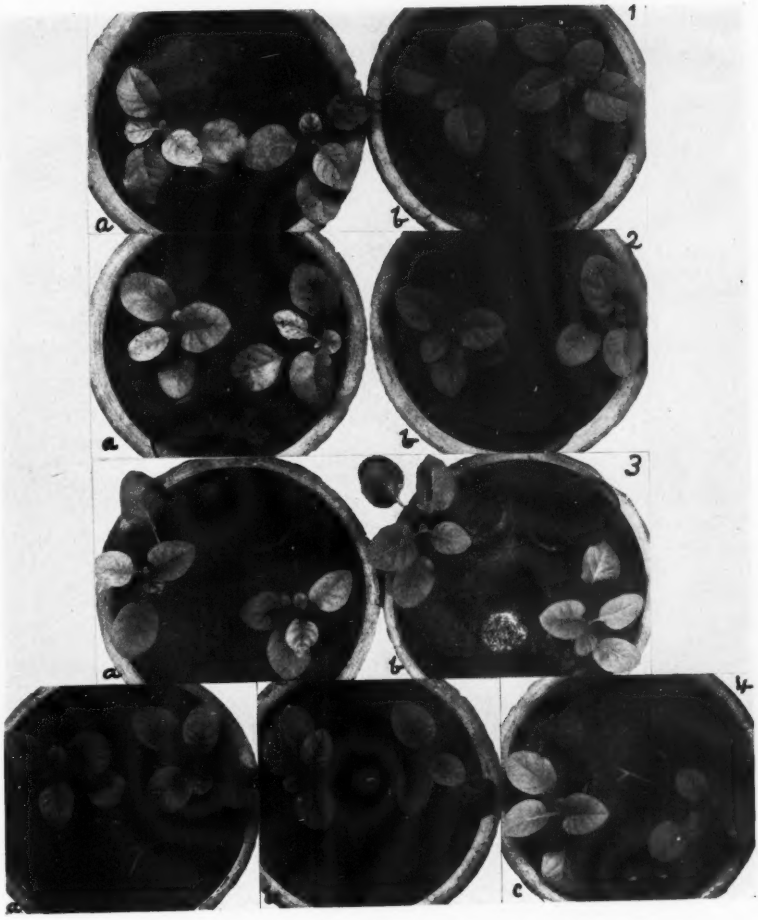
PLATE 1

Toxic Condition in Turkish Tobacco Plants 10 Days After Being Set; Considerable Chlorosis in Unlimed Soils; None in Limed Soils

Fig. 1. Berea soil: a, check soil; b, limed soil.
Fig. 2. Greenville soil: a, check soil; b, limed soil.
Fig. 3. Campbellsville soil: a, check soil; b, limed soil.
Fig. 4. Mayfield soil: a, check soil; b, superphosphated soil; c, limed soil.



FIGS. 1–4

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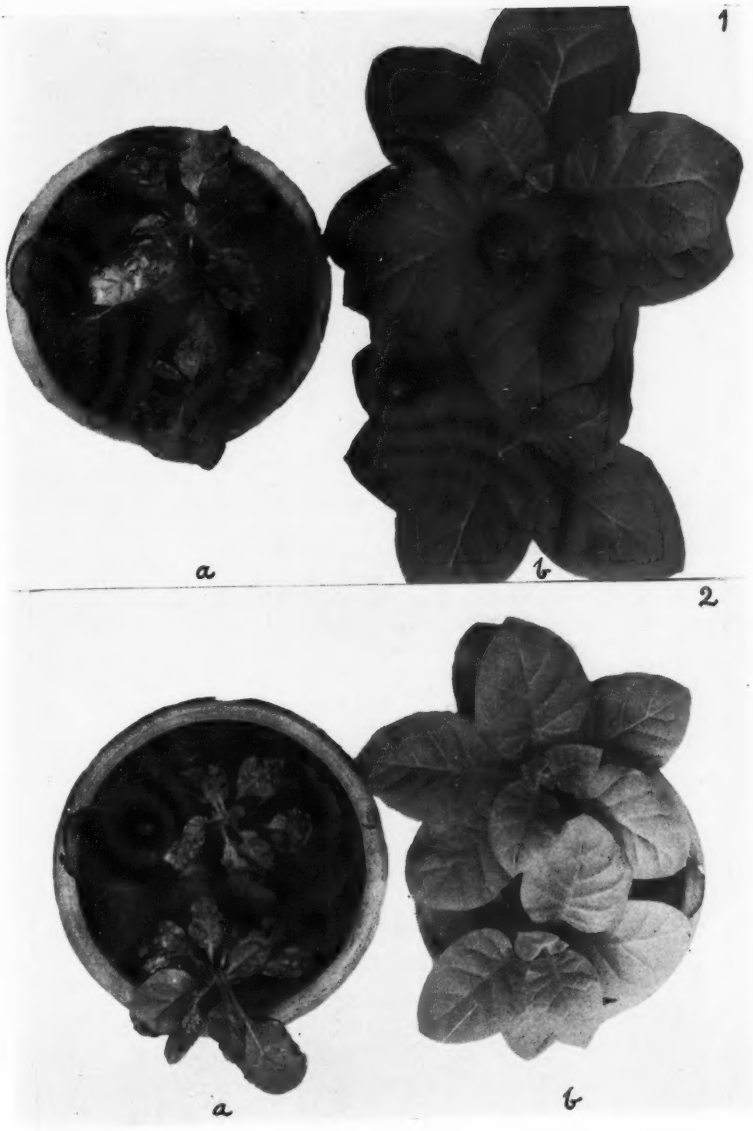
PLATE 2

SEVERE TOXIC CONDITION IN TURKISH TOBACCO 49 DAYS AFTER BEING SET; NO TOXICITY IN LIMED SOILS

FIG. 1. Berea soil: a, check soil; b, limed soil.

FIG. 2. Greenville soil: a, check soil; b, limed soil. Phosphorus-deficient spotting on two leaves.



FIGS. 1–2

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PLATE 3

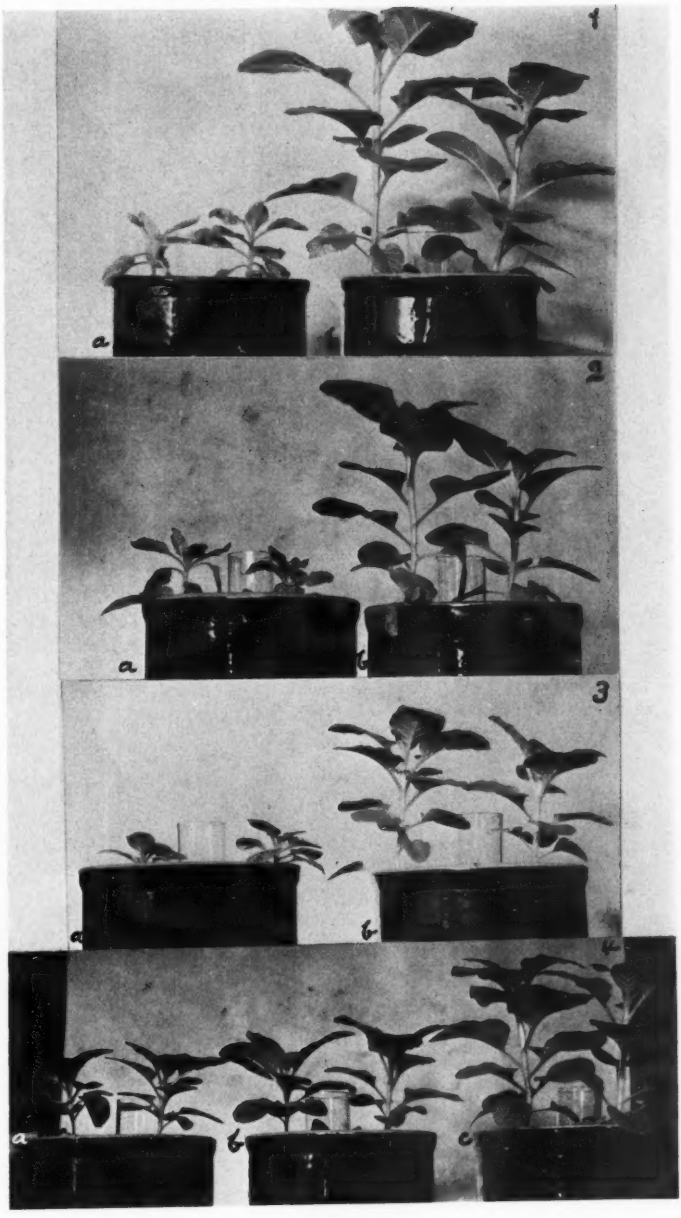
TURKISH TOBACCO PLANTS, 49 DAYS AFTER BEING SET, SHOWING COMPARATIVE SIZE, TOXIC CONDITION IN PLANTS FROM BEREA AND GREENVILLE CHECK SOILS, AND RECOVERY IN THE CAMPBELLSVILLE AND MAYFIELD UNLIMED SOILS; NO TOXICITY IN THE LIMED SOILS

FIG. 1. Berea soil: a, check soil; b, limed soil.

FIG. 2. Greenville soil: a, check soil; b, limed soil. The lower leaves on these plants as well as those in figure 1b show spotting due to phosphorus deficiency.

FIG. 3. Campbellsville soil: a, check soil; b, limed soil.

FIG. 4. Mayfield soil: a, check soil; b, superphosphated soil; c, limed soil.



FIGS. 1–4

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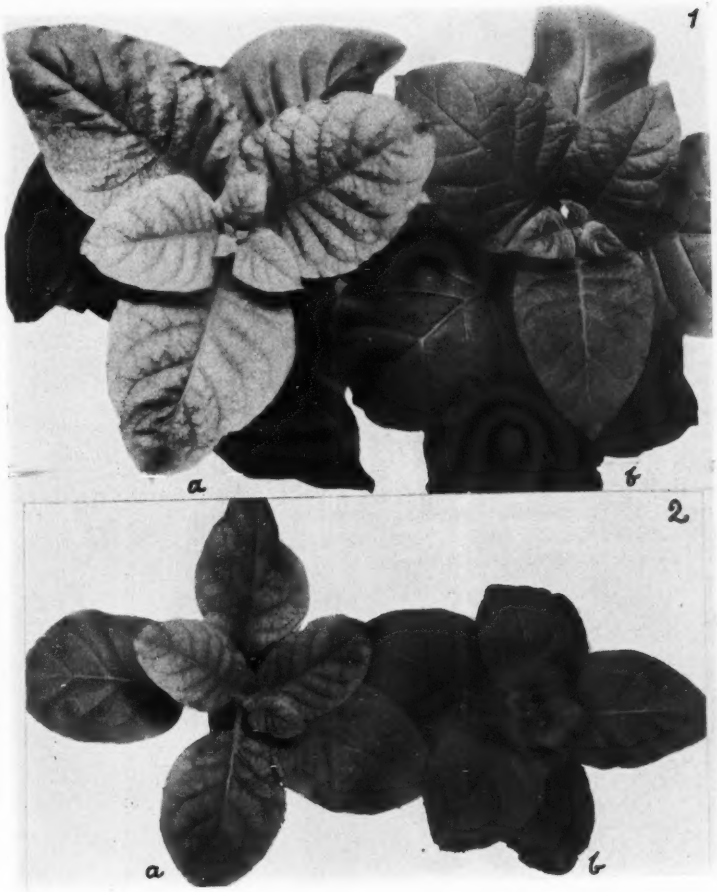
PLATE 4

TOXIC CONDITION OF TURKISH TOBACCO IN WATER CULTURES CONTAINING MANGANESE: PHOTOGRAPHED 13 DAYS AFTER Mn ADDITIONS

FIG. 1. Plants from Experiment 2: (a) Full nutrient solution plus 40 p.p.m. of Mn. Severe chlorosis with brown necrotic areas. (b) Full nutrient solution; no Mn. No chlorosis.

FIG. 2. Plants from Experiment 3, showing effect of phosphorus in reducing manganese injury: (a) Nutrient solution containing no phosphorus, plus 15 p.p.m. of Mn. Severe chlorosis with some necrotic areas. Phosphorus deficient spot on one leaf. (b) Full nutrient solution plus 15 p.p.m. of Mn. Slight chlorosis in growing point.



FIGS. 1–2

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PLATE 5

EFFECT OF SUPPLEMENTARY PHOSPHATE TREATMENTS IN OVERCOMING THE TOXIC CONDITION IN TURKISH TOBACCO GROWN IN BEREA AND GREENVILLE CHECK SOILS; PHOTOGRAPHED 48 DAYS AFTER THE FIRST TREATMENT WAS ADDED

FIG. 1. Berea soil: (a) Two 1-gm. additions of $Na_3PO_4 \cdot 12H_2O$. Some chlorosis in growing point. (b) No phosphorus additions. Severe toxic condition.

FIG. 2. Greenville soil: (a) Two 1-gm. additions of $Na_3PO_4 \cdot 12H_2O$. No chlorosis. (b) No phosphorus additions. Severe toxic condition.

FIGS. 1–2

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MINERAL CONSTITUENTS IN RELATION TO CHLOROSIS OF ORANGE LEAVES

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Chlorosis or yellowing of orange leaves has been observed in many of the orange groves in the Gosford district, N. S. Wales, for several years, and is gradually becoming more prevalent. The affected leaves first show diffused yellow interveinal areas, not specially demarcated from the green tissue and rather toward the petiole end of the leaf. Gradually the whole leaf assumes a yellow color, with a greenish tinge along the main veins and midrib, but these eventually become yellowish. The chlorotic leaves tend to occur more on the northern or northwestern aspects of the trees, those aspects receiving the greatest intensity of light. The affected leaves are narrower than normal leaves, and in moderately affected trees sometimes occur in patches confined to individual limbs. In badly affected trees, yellow leaves are distributed over the whole surface. No bunching of small twigs accompanies the disease, but a marked abscission of yellow leaves takes place during the winter months.

Chlorosis and mottling of orange leaves have been reported from many parts of the world, though usually ascribed to conditions other than those that obtain at Gosford.

Chlorosis is a diseased condition of plant leaves induced by some abnormality in the supply of nutrients, which results in a failure to produce a normal amount of chlorophyll, and thereby the amount of material synthesized by affected leaves is reduced. Compounds of nitrogen, iron, and magnesium are intimately associated with the production of chlorophyll (17), and frequently when soil conditions are such as to render the uptake of these substances insufficient for plant requirements a chlorotic condition is produced.

Hilgard (8) reports a yellowing of the leaves and general unthriftiness of citrus trees grown on Californian soils which have an accumulation of calcium carbonate in the subsoil. The alkalinity of these soils evidently results in the immobilization of iron compounds, and a chlorotic condition resulting from a lack of iron ensues. Many methods have been used to overcome a lack of iron in citrus (2, 15). Thomas and Haas (14) found that soil applications of sulfate of iron up to 100 pounds per tree had no effect. When aged Valencia trees were injected with 2 liters of water containing 10 gm. of iron tartrate, a marked abscission of the yellow leaves resulted, followed by new growth from the axillary buds. The new growth was of normal color, and fruit production

increased, but in less than 2 years the leaves of the succeeding cycles of growth were of pale color, indicating the temporary nature of the improvement.

Kelley and Thomas (11) describe the effect of alkali on orange trees—on some soils mottle-leaf is one of the early symptoms, whereas trees on soils containing specially high concentrations of sulfates and bicarbonates exhibit a chlorotic condition similar to that referred to by Hilgard on calcareous soils.

COLLECTION OF SAMPLES

Some difficulty was experienced in locating trees which were totally free of evidences of chlorosis, for such trees form a very decided minority in the various groves visited. Samples of leaves were collected on November 24, 1931, at a time when there was little new growth on the trees. Since care was taken to avoid young leaves, the material collected represents mature leaves ranging in age from probably several months to 2 years or over. From 200 to 300 leaves were collected from a tree, and each sample represents leaves from a single tree. There are very notable differences in the composition of immature and mature orange leaves. Young leaves contain very much higher percentages of phosphorus, iron, potash, and nitrogen than do old leaves (10), and there is a gradual diminution of these constituents as growth proceeds. The calcium content is exceptional in that it is low in young leaves and increases in amount until full maturity is reached.

The leaves were washed individually, air dried, and then ground in a hand mill and stored in bottles. The petioles were not included in the prepared samples. In table 1 a description of the samples is given.

Soil samples were collected from holes dug within several feet of the trees, and are given numbers corresponding to the number given the leaf samples of the respective trees. Soils in the Gosford district range from dark-gray to yellowish loamy sands or sandy loams, passing into the B horizon at 18 to 20 inches. The latter consists of yellowish-brown or orange loams, or clayey sands, which overlie sandstone, or ferruginous indurated sandstone.

The samples consist of A1 and A2 horizons to a depth of 18 to 20 inches. The largest portion of the trees' roots is in this zone, for there is a decided tendency for the longer roots to run above and parallel to the B horizon.

THE SOILS AT GOSFORD

A general reference to the soils at Gosford with respect to profile characteristics has already been made. One can well deduce the type of soils from a consideration of the climatic conditions. Moderate temperatures combined with a 45-inch rainfall have resulted in the light-textured soils derived from sandstone being very much leached and strongly acid in reaction; pH values of 4.2 are frequently encountered. The topography is steep to rugged with valley alluvium, and where soil has been sufficiently long in situ, it has devel-

oped strongly podzolic characters, but considerable areas of the soils are of the nature of truncated podzols and consist largely of soils representing B hori-

TABLE 1

Description of the leaf samples

GROVE	SAMPLE NUMBER	VARIETY	NATURE OF LEAF SAMPLES
W. Holcombe	1*	Valencia	Green leaves from healthy tree
	2	Valencia	Green leaves from healthy tree
	3	Valencia	Yellow leaves from affected tree
	4	Valencia	Yellow leaves from affected tree
	5	Valencia	Green leaves from healthy tree
	6	Valencia	Green leaves from healthy tree
E. A. Bailey	7	Washington Navel	Green leaves from badly affected tree
	7A	Washington Navel	Yellow leaves from same tree as 7
	8	Washington Navel	Green leaves from badly affected tree
	8A	Washington Navel	Yellow leaves from same tree as 8
	9, 10	Washington Navel	Green leaves from adjacent trees, showing slight evidences of yellowing
	11	Valencia	Yellow leaves from badly affected tree
	12	Valencia	Green leaves from healthy tree
H. Westcott	13	Valencia	Yellow leaves from badly affected tree
	14	Valencia	Yellow leaves from badly affected tree
	15	Washington Navel	Yellow leaves from affected tree
	16	Washington Navel	Green leaves from tree showing trace of yellowing
N. Scholer	17	Valencia	Yellow leaves from badly affected tree
	18	Valencia	Yellow leaves from badly affected tree
N. E. Pinkston	19	Valencia	Green leaves from tree showing trace of yellowing
	20, 21	Valencia	Green leaves from younger healthy trees 7 to 8 years old
	La, LB	Valencia	Green leaves from healthy trees at Leeton, Murrumbidgee Irrigation Area, N.S.W.

* Trees 1–6 are located in a fertilizer experiment (3) and have annually since 1925 received the following treatment per tree:

1 and 2. 5 pounds bone dust, 5 pounds superphosphate, 4 pounds sulfate of potash, 9 pounds sulfate of ammonia.

3 and 4. The same as 1 and 2, but with only 4 pounds sulfate of ammonia.

5 and 6. The same as 1 and 2, but with potash omitted.

zons of former soils. Table 4 gives the reaction, nitrogen, and replaceable base content of soils numbered to correspond with trees from which leaf samples were taken.

DISCUSSION

In comparing the chemical composition of chlorotic leaves with normal leaves, many similar features present themselves in widely varying plant families. Wallace and Mann (16), in their investigations of lime-induced chlorosis of apple trees, found that there was a higher ash, potassium, and sodium (especially potassium) content in the chlorotic leaves; a much higher content of calcium, together with a somewhat greater magnesium content in the green leaves, whereas the amounts of iron, aluminum, phosphorus, and silica were not greatly different. The author in unpublished data has compared the composition of normal and chlorotic peach leaves of the same variety, the diseased trees being located on an area at Leeton, Murrumbidgee Irrigation Area, on which a previous citrus crop had developed chlorosis. There was a higher ash, potassium, sodium, manganese, phosphorus, and silica content in the yellow leaves, and higher lime and nitrogen content in the green.

Haas, Batchelor, and Thomas (6) report that "yellows" or "little-leaf" of walnut trees, rosette of pecan trees, as well as little-leaf of peach, and mottling of apricot have been found to be independent of nitrogen requirements, cultural practices, and nematode infection, but appear to be dependent on the base relationship existing in the soil. The ash of the affected leaves is lower in calcium and higher in potassium than that of healthy leaves of the same age.

Comparing the composition of normal and mottled orange leaves, Kelley and Cummins (10) found that mottled leaves contained greater amounts of potassium, phosphorus, magnesium, sulfate, and nitrogen. Normal leaves contained a greater amount of calcium, whereas the iron, silica, and chlorine contents did not materially differ.

Neither in the symptoms of mottle leaf as it occurs in California (4) and in chlorotic leaves at Gosford nor in the relation of the diseases to normal leaves in the same locality are there many parallel features. In the former, irregular spots several millimeters in diameter appear between the larger veins and may become larger and more numerous until the only chlorophyll remaining is confined to the midrib and main veins. A specific feature is that the areas surrounding the yellow spots retain their normal green color, at least till the spots embrace a large proportion of the leaf. In the Gosford samples the percentage of potassium is significantly higher in the chlorotic leaves than in the green leaves of normal trees. Of the latter 9 and 10 are exceptional in having a relatively high potassium content but have as yet not developed any considerable degree of chlorosis. They are, however, situated near trees which show much evidence of yellowing, and the disease will probably soon become more marked. It appears that a high potassium content may precede a serious manifestation of the disease. Of the chlorotic leaves 13 and 14 are exceptional in that they do not have a high potassium content. It is, therefore, a usual but not a necessary accompaniment of chlorosis that leaves have a high potassium content. A low potassium content associated with yellowing may

TABLE 2

Composition of green leaves from healthy or slightly affected trees

Ash, constituents of ash, and nitrogen, expressed as percentage of dry matter

NUMBER	VARIETY	ASH	SiO_2	CaO	MgO	K_2O	Na_2O	MnO	Fe_2O_3	SO_4	Cl	P_2O_5	N
1	Valencia	13.23	.413	6.36	.314	0.772	.156	.0018	.066	.371	.121	.236	2.26
2	Valencia	13.16	.328	6.31	.403	0.706	.191	.0020	.043	.414	.113	.227	2.26
5	Valencia	14.30	.415	7.10	.471	0.495	.253	.0016	.039	.475	.112	.229	2.22
6	Valencia	13.92	.350	6.73	.536	0.445	.238	.0018	.033	.418	.115	.241	2.28
12	Valencia	12.56	.352	5.66	.860	0.562	.196	.0011	.055	.451	.103	.198	2.17
19	Valencia	10.30	.171	4.84	.186	0.788	.228	.0007	.035	.409	.103	.213	2.21
20	Valencia	14.81	.191	7.08	.379	0.992	.385	.0014	.030	.398	.123	.230	2.15
21	Valencia	14.48	.196	7.12	.330	0.925	.349	.0011	.033	.370	.123	.229	2.16
9	Washington Navel	12.38	.660	4.84	.351	1.492	.307	.0015	.061	.581	.168	.264	2.38
10	Washington Navel	11.74	.660	5.06	.286	1.425	.304	.0020	.056	.619	.128	.233	2.19
16	Washington Navel	12.02	.375	5.97	.386	0.768	.324	.0022	.036	.582	.172	.232	2.57
LA*	Valencia	13.55	.721	5.40	.780	0.721	.112	.0023	.081	.772	.021	.259	2.26
LB*	Valencia	12.17	.678	5.14	.627	0.830	.197	.0019	.126	.667	.027	.241	2.43
Mean.....		13.05 ±.251	.366 ±.058	6.11 ±.164	.410 ±.031	0.864 ±.181	.264 ±.012	.0015 ±.000025	.044 ±.0024	.462 ±.017	.125 ±.0046	.230 ±.0034	.227 ±.0023

* Not included in mean.

TABLE 3

Composition of chlorotic and green leaves from trees showing chlorosis

Ash, constituents of ash, and nitrogen, expressed as percentage of dry matter

NUMBER	VARIETY	ASH	SiO_2	CaO	MgO	K_2O	Na_2O	MnO	Fe_2O_3	SO_4	Cl	P_2O_5	N
3	Valencia	13.60	.666	5.93	.103	1.383	.334	.0030	.048	.398	.186	.237	1.94
4	Valencia	13.28	.638	6.13	.114	1.176	.395	.0013	.042	.425	.248	.238	2.04
11	Valencia	13.70	.453	6.64	.052	0.943	.299	.0012	.045	.462	.202	.229	2.15
13	Valencia	11.69	.437	5.52	.062	0.725	.263	.0028	.043	.546	.187	.213	2.28
14	Valencia	12.72	.578	6.41	.052	0.613	.317	.0033	.040	.624	.232	.210	2.13
17	Valencia	12.62	.385	6.14	.052	1.043	.395	.0006	.033	.786	.132	.285	1.86
18	Valencia	13.17	.358	6.36	.044	1.051	.333	.0007	.037	.404	.152	.245	1.77
7	Washington Navel	13.32	.395	5.85	.213	1.603	.189	.0014	.049	.423	.180	.249	2.38
7A	Washington Navel	14.84	.604	6.12	.079	2.223	.386	.0022	.040	.485	.186	.231	2.07
8	Washington Navel	13.25	.438	5.40	.151	1.728	.249	.0015	.060	.548	.126	.256	2.38
8A	Washington Navel	13.44	.515	4.93	.099	2.475	.416	.0015	.055	.437	.153	.282	2.22
15	Washington Navel	11.74	.536	5.70	.047	0.943	.341	.0018	.052	.406	.213	.159	2.21
Mean.....		13.08 ±.156	.508 ±.021	5.93 ±.093	.096 ±.0108	1.300 ±.109	.327 ±.013	.0018 ±.00015	.045 ±.0014	.495 ±.023	.178 ±.0069	.235 ±.0065	2.12 ±.0054

ensue from a limited soil potassium supply, but the latter condition in relation to the disease does not appear to be causal.

Bartholomew and Janssen (1) have shown that plants will absorb large amounts of potassium, apparently in excess of that required for normal growth, when excessive amounts are made available. Under these conditions potassium does not enter into organic combinations but remains in a water-soluble condition.

The same authors (9) working with tomatoes in nutrient solution found that nitrogen and potassium bear an inverse relationship in that wherever a high percentage of potassium is found in the plants a low percentage of nitrogen is likely to occur.

Though there is in general a higher potassium and a lower nitrogen content in the yellow leaves, individual considerations do not support the theory that the high potassium content of the yellow leaves may be due wholly to an insufficient nitrogen supply.

In considering the composition of leaves 1–6, some effects apparently due to the fertilizer treatment can be deduced. Trees 1 and 2 have received potassic fertilizer and relatively high amounts of nitrogen. Trees 3 and 4 have received the same amount of potassium but less than half the amount of nitrogen; there has been a considerably greater uptake of potassium by the yellow leaves together with a much diminished amount of magnesium and somewhat less nitrogen. Trees 5 and 6 have received no potassium but the same amount of nitrogen as 1 and 2; the leaves are normal, the potassium content is low but the magnesium content is high and no disease symptoms have attended the withholding of potassium supplies. Reed and Haas (13) in experiments with orange trees grown in nutrient solutions found that orange trees can function with considerably less potassium than they ordinarily absorb, and young trees grow fairly well over an experimental period of 17 months in a solution devoid of potassium, being able to subsist on the potassium contained in their tissues at the outset of the experiment. The effect of fertilizer treatment on 3 and 4 does suggest that a low nitrogen supply has contributed to disease conditions and high potassium content, and especially to a feature common to all the samples of chlorotic leaves, namely, a low content of magnesium. The magnesium deficiency of chlorotic leaves is the most striking feature in a comparison of their composition with normal leaves.

The mean content of magnesium in the normal leaves is 0.41 ± 0.0313 per cent and that of chlorotic leaves 0.096 ± 0.0108. No. 19 represents the normal foliage of a tree in the same grove as 20 and 21, though the latter are younger trees, and on soil that has been under cultivation for a shorter period. The magnesium content has fallen to a lower figure in the older tree, whereas in the younger trees the magnesium content is fairly high. Coincident with the low magnesium content of the older tree is the early appearance of yellow leaf; the effects of continued cropping and soil impoverishment are reflected in the low total mineral content.

A good deal of prominence has of late years been given to the rôle of magnesium as a limiting factor in plant nutrition, and specific diseases have been attributed to the lack of this constituent. Chucka (5) reports that a chlorotic appearance of potatoes, known as "potato sickness," could be prevented by the addition of magnesium to potato fertilizers. McMurtry (12) reports that when magnesium is deficient in tobacco soils, the deficiency gives rise to a chlorosis of tobacco leaves, which is usually worse on sandy soils. The specific symptoms of magnesium deficiency in regard to tobacco is the loss of the green color at the tip and margins of the lower leaves of the plant—in some cases the lower leaves of the plant may be almost white.

In 7 and 7A and 8 and 8A a comparison is made of the composition of green and chlorotic leaves derived from trees showing a diseased condition. The green leaves show the same general features of the mineral content of chlorotic leaves especially in an abnormal potassium content, but the abnormalities are greatly accentuated in the yellow leaves. The magnesium content of the green leaves is low but in the yellow leaves is considerably less. There are no significant differences in the ash, calcium, iron, sulfate, or phosphate contents of the normal and diseased leaves.

There is a higher content of silica, sodium, and chlorine in the yellow leaves. The manganese content of the latter is also higher but in a barely significant degree. There is a slightly higher nitrogen content in the normal leaves.

LA and LB are two samples of healthy Valencia orange leaves collected from two trees in a grove at Leeton, Murrumbidgee Irrigation Area, N. S. Wales. They were included in the analyses for comparison with leaves from healthy trees at Gosford. These two districts are very dissimilar in climatic, and consequently soil, conditions. Despite the more basic nature of the soils at Leeton, the composition of the leaves is similar to those at Gosford, viz., comparatively low potassium and sodium, high magnesium, similar nitrogen and phosphorus, and a very low chlorine content.

Some interest attaches to the high chlorine content of chlorotic leaves, and a tendency to a higher sulfate content than leaves of normal trees. Haas and Thomas (7) report injuries to the leaves of lemons as a result of the accumulation of sulfur compounds, and that the use of generous additions of nitrogenous fertilizers somewhat decreases the toxic effects due to sulfate and chloride concentration in the leaves by increasing the leaf area.

An examination has been made of the replaceable magnesium, calcium, and potassium, of the soils corresponding to the leaf samples, to determine whether there is any correlation between the amount of replaceable bases and the amount of bases occurring in the leaves of the trees, especially where a deficiency occurs in the leaves.

The replaceable calcium content of the soils is low throughout, and very low in many samples. It corresponds with amounts of this base found in light-textured acid soils in other parts of the world, or in light-textured acid soils from which calcium has been largely lost by the use of ammonium salts as a

fertilizer. Since ammonium sulfate is a cheap and effective source of nitrogen in citrus fertilizer practice, the already low calcium content will become aggravated. Citrus trees contain notably large amounts of calcium in comparison with other crop plants, and there is a distinct possibility of a calcium hunger being induced on these soils. Oranges are grown in many parts of the world under semi-arid conditions, and in soils rich in bases. In considering the vastly different conditions at Gosford—leached, acid, base-poor soils—it is evident that much stronger influences than the amount of nutrients available to a plant govern its composition, and the most potent factor would appear to be heredity.

TABLE 4

Reaction, nitrogen, and replaceable base content of soils

SOIL NUMBER	NITROGEN	pH	REPLACEABLE BASES EXPRESSED AS M.E. PER 100 GM.		
			CaO	MgO	K_2O
	per cent				
1	.105	5.3	3.38	.505	.343
3	.092	5.0	2.67	.359	.242
4	.085	4.8	2.18	.288	.226
5	.104	4.8	2.48	.288	.191
7	.085	4.2	1.08	.324	.189
8	.088	4.2	1.69	.281	.275
9	.101	4.6	1.72	.327	.416
11	.137	4.6	2.10	.395	.327
12	.143	5.2	3.57	.891	.245
13	.083	4.4	1.38	.308	.159
15	.110	4.9	1.30	.184	.104
16	.120	4.4	1.92	.381	.127
17	.051	5.0	1.24	.266	.085
19	.046	5.3	1.50	.137	.077
20	.053	5.3	1.81	.252	.119

Though in these soils the amount of bases is such that almost no single one can be very remote from being a limiting factor, there is no significant degree of correlation between the available bases of the soils, as measured by their replaceability, and the amounts of those bases occurring in the leaves.

The magnesium content is also low and typical of leached acid soils. The soils containing most magnesium are associated with trees whose leaves have a high magnesium content, as those containing least are associated with chlorotic trees, but considering the whole series there is no significant correlation.

A few of the soils appear moderately well supplied with potassium, but the majority have small reserves of this base. Iron appears to be in a sufficiently mobile condition in these soils, for an appreciable amount is extracted by a normal solution of ammonium chloride.

SUMMARY

Chlorosis of orange trees is becoming an increasingly serious disease at Gosford, N. S. Wales. The symptoms of the disease are described.

Analyses of normal leaves from healthy or very slightly affected trees, and of chlorotic leaves are given.

The salient feature in comparing the mineral composition of healthy and diseased leaves is the deficiency of magnesium in the latter.

The normal leaves have a significantly greater content of magnesium and nitrogen.

The content of potassium, sodium, silica, and chlorine is higher in the chlorotic leaves. Ash, calcium, manganese, iron, sulfate, and phosphate contents are not significantly different.

The composition of normal orange leaves grown under vastly different soil and climatic conditions differs little from normal leaves grown at Gosford.

Soil conditions at Gosford are briefly discussed, and the major replaceable base constituents of a number of soils are given.

There is no significant degree of correlation between replaceable bases in these soils, and the uptake of the corresponding bases.

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CARBON DIOXIDE PRODUCTION BY MANNITE-TREATED SOILS AS A MEANS OF DETERMINING CROP RESPONSE TO FERTILIZERS

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Since running field fertilizer tests on all soil types and on all parts of the same soil which have different fertilizer needs is impracticable, investigators have developed rapid laboratory methods for determining soil deficiencies. Certain investigators have used the rate of evolution of carbon dioxide as a measure of the activity of the soil microörganisms. This method has the advantage over some biological methods in that the determinations are quantitative. Soil microörganisms not only require an energy-giving material, but they also require approximately the same nutrients which crop plants require. The activity of the soil microörganisms in the presence of an energy material, and therefore the rate of evolution of carbon dioxide, should be a function of the nutrients available for crops, other growth factors being taken care of.

Waksman and Starkey (5) found that soils could be graded on a basis of their fertility by determining the amount of carbon dioxide formed by 1 kgm. of fresh soil in 14 days or by determining the amount of carbon dioxide produced in 48 hours by 100 gm. of fresh soil to which 500 mgm. of dextrose had been added, as well as by determining the numbers of microörganisms and the nitrification.

Waksman and Heukelekian (3) found that when cellulose was added to a soil 40 to 50 mgm. of cellulose was decomposed in 14 days for every milligram of available nitrogen present. They measured the decomposition of the cellulose by determining the carbon dioxide evolved.

Corbet (2) and numerous others have determined the effect of the addition of various fertilizing salts on the rate of evolution of carbon dioxide by a soil. Usually they did not add an energy material to the soil; consequently, the increases in carbon dioxide obtained were either negligible or small.

Waksman and Karunakar (4) found that information concerning the microbiological flora capable of fixing nitrogen and concerning the available phosphorus in a soil could be obtained by the following methods:

[1] Acknowledgment is made to C. B. Anders, leader in soils, Mississippi, for fostering the project and for helping to obtain soil samples; to the soils staffs of the Louisiana, Texas, and South Carolina Experiment Stations for supplying field data and soil; to S. A. Waksman of New Jersey; to Roland Cowart, J. B. Edmond, C. B. Anders, and W. W. Hull of Mississippi; and to A. H. Meyer of the Louisiana Experiment Station, for criticizing the manuscript.

1. "The common solution method, consisting in adding 1 or 5 gm. of soil to a standard mannite solution, incubating for 7 to 28 days, then determining the increase in total nitrogen above the control. This serves as an index of the nitrogen fixing flora of the soil and to some extent of the microbiological condition of the soil.

2. "The method suggested by Niklewski (—) and Stoklasa (—). This consists in adding 10 gm. of the particular soil to 100 cc. of 2 per cent mannite solution, free from available phosphates, sterilizing and inoculating with a vigorous culture of azotobacter. After incubating for 20 to 30 days, the increase in total nitrogen is determined. This can serve as an index of the available phosphate in the soil.

3. "The method for determining residual mannite (or rather soluble organic matter) in the soil suggested by Christensen (—). This consists in adding 2 per cent of mannite to the soil, incubating with optimum moisture, then determining the residual mannite every five days by oxidation with $KMnO_4$. This method as well can serve as an index of the activities of the nitrogen fixing flora and of the amount of phosphorus available in the soil."

Waksman and Karunakar concluded that nitrogen fixation on mannite treated soil is an unreliable index of microbiological activity because the quantities of nitrogen are small and the methods for determining nitrogen are not sufficiently sensitive to measure them. They found much more applicable the method of Christensen in which mannite disappearance is measured.

In the South, nitrogen and phosphorus are the nutrients must often deficient in the cultivated soils. All microbiological methods in soil investigation are based upon the fact that crop plants and soil microörganisms require similar nutrients for their development: the plants obtain their energy from the sun, and the lower organisms obtain theirs from energy-giving compounds.

The main differences in the method suggested by Christensen and the method proposed in this paper are: (*a*) Christensen used water on the soil equal to 75 per cent of the maximum water-holding capacity of the soil, whereas in the method proposed in this paper 33⅓ per cent of the maximum water-holding capacity is used; (*b*) Christensen determined the residual mannite, whereas in the method of this paper the carbon dioxide, an end product of respiration, is determined; (*c*) the determinations required by Christensen's method are one every 5 days until 30 days have passed, whereas only one determination and 1 day are required by the proposed method.

The water used by Christensen, which is much greater than that which the plants under usual cultivation conditions are subjected to for any length of time, is sufficient to influence markedly the solubility of the soil phosphates, and it is reasonable to assume that maintenance at this moisture content for some time will alter the absorption of phosphorus from the soil by the microörganisms.

The moisture used in the proposed method is 33⅓ per cent of the maximum water-holding capacity, and the soil is friable and loose as in a freshly cultivated field. The conditions as to moisture and air are similar to those of a freshly cultivated field.

When mannite or any readily available energy material is added to the soil the conditions are made as favorable for the soil microörganisms as for crop plants. If sufficient nutrients are available, both the production of CO_2 by the

soil microörganisms and the crop yield will be large. If nitrogen or phosphorus is deficient in a soil the addition of the deficient element to a field will increase the crop yield, likewise its addition to a mannite-treated soil will increase the production of CO_2 by the soil microörganisms.

The time (24 hours) required in the proposed method is sufficiently long for responses to nitrogen and phosphorus to show up and sufficiently short to prevent the nitrogen fixed by the soil flora from markedly affecting the production of CO_2.

Waksman and Starkey (5), Waksman and Heukelekian (3), Christensen and Jensen (1), and Corbet (2) have reviewed the literature relative to carbon dioxide production and microbiological analysis of the soil.

The object of the investigation reported here was to determine the relationship between the activity of the soil microörganisms in the soil to which mannite had been added, as measured by CO_2 production, and the fertilizer requirement of the soil for cotton production as measured by crop yields.

For the laboratory work in this investigation soil samples were collected from 13 different experimental fields in Mississippi and Louisiana on which fertilizer tests for cotton had been, or were being, conducted and for which crop yields are available. The samples of soil were taken from the unfertilized plots where the experiment was still in progress and at random over the field where the experiment had been discontinued. In the laboratory after preliminary tests the following ingredients were added to duplicate 100-gm. samples of air-dry soil:

1. 500 mgm. mannite.
2. 500 mgm. mannite and 30 mgm. of nitrate of soda for the Mississippi soils, or 25 mgm. for the Louisiana soils.
3. 500 mgm. mannite, nitrate of soda,[2] and 25 mgm. superphosphate.

After the soil and the added ingredients had been thoroughly mixed, water equal to 33⅓ per cent of the maximum water-holding capacity of the soil was added. The maximum water-holding capacity was taken as that amount of water which is retained in a soil in a filter funnel when water is added in excess, and the excess allowed to drain off. The soil so treated was then pulverized, care being taken to distribute the moisture uniformly, after which it was put into 1,000-cc. Erlenmeyer flasks. The flask was closed with a 2-hole rubber stopper carrying a long glass tube extending to the bottom of the flask and a short glass tube extending just through the stopper. The flask was made airtight by putting over the outer ends of the tubes rubber tubes closed at one end with pointed glass stoppers. Glass wool was put over the inside end of the short glass tube to exclude the soil. Then the flask with its contents was inverted into its support and incubated for 24 hours at room temperature in summer and at 30°C. in winter. After the incubation period of 24 hours the flask was connected in a gas train for the collection of the carbon dioxide. The members of the train in order were: soda lime column, soil flask, H_2SO_4 tube, $CaCl_2$ tube (improvised), ascarite tube (improvised from a 1-inch by 6-inch

[2] See number 2 for the quantity.

test tube, a 2-hole rubber stopper, and glass tubing), $CaCl_2$ tube, and a 3,600-cc. water bottle from which water was siphoned in order to draw air through the train. The soil flask was so connected that the air entered it through the long tube and passed downward through the soil and out through the short tube thus facilitating the removal of the carbon dioxide.

The carbon dioxide was swept out of the soil flask by drawing 3,600 cc. of CO_2-free air through the train. The CO_2 was absorbed by the ascarite and determined by weighing the ascarite tube before and after the absorption. The ascarite tubes were stored in $CaCl_2$ desiccators when not in use. The change in weight of the tube between one determination and the next was not sufficient to require weighing again if the period was only a few days.

The Mississippi field fertilizer tests have a check plot after each three plots. The yields of the check plots were interpolated to determine the check yields of the plots between the checks. The increases in carbon dioxide obtained in the laboratory as a result of the addition of nitrogen and of nitrogen plus phosphorus were compared with the following field tests: 600 pounds 6–0–0 and 600 pounds 6–8–0, except in the case of Houston clay where the nitrogen was 8 per cent instead of 6. Both the field and laboratory data are reported as increases over no fertilizer. The no fertilizer yields of seed cotton and the carbon dioxide produced without fertilizer are also reported. The laboratory data reported are usually an average of duplicate determinations. The agreement of the duplicate determinations usually approach that of duplicate quantitative chemical determinations. The increase for phosphorus was obtained by subtracting the increase for nitrogen from the increase for nitrogen plus phosphorus in both the field and laboratory data. No response was obtained for muriate of potash in the laboratory under any conditions, and very little was obtained for phosphorus when added without nitrogen.

RESULTS

The Mississippi soils were collected in July and air dried, and the laboratory determinations were made soon afterwards. The odds were calculated for the field data by the use of Student's method. The data for the Mississippi soils are reported in table 1 and figure 1. The scale used in figure 1, 1 mgm. of CO_2 = 4 pounds of seed cotton, was chosen so that the lines representing increases in seed cotton and those representing increases in CO_2 would fall as closely together in the figure as possible. In setting up an arbitrary scale of this kind the assumption is made that the factors other than nitrogen and phosphorus have been equally distributed in all cases, but it is quite well known that nature does not do things that way when only a few years are involved.

Orangeburg fine sandy loam.—The field test was conducted only 1 year. On this year the increases due to fertilizer were larger than would be obtained over a 5-year average. When the data are considered as they stand, nitrogen produced an increase of 559 pounds of seed cotton and phosphorus produced an increase of 33 pounds; the increases in CO_2 in the laboratory indicate increased yields

TABLE 1

The response of cotton and soil microörganisms to nitrogen and to nitrogen and phosphorus

SOIL TYPE	LOCATION	pH*	FIELD DATA‡	LBS. SEED COTTON PER ACRE						MGM. CARBON DIOXIDE			
				Yield, no fertilizer	Increase		Increase		Increase	Yield without fertilizer	Increase		
					N over none	Odds	NP over N	Odds	N and P over none		N	NP over N	NP
Houston clay	Prairie, Miss.	6.7	12	501	8	1:1	385	1110:1	393	51	9	70	79
Ruston fine sandy loam	Columbus, Miss.	6.5	12	290	397	9999:1	174	9999:1	571	November 22	82	23	105
										July 25	54	52	106
Orangeburg fine sandy loam	Macon, Miss.	7.4	2	230	559	24:1	33	4:1	592	32	112	7	119
Norfolk fine sandy loam	Macon, Miss.	6.1	9	560	179	9999:1	194	2999:1	373	28	80	49	129
Oktibbeha clay	Macon, Miss.	5.9	6	343	26	3:1	297	1666:1	323	46	23	44	67
Sarpy fine sandy loam	Stoneville, Miss.	6.2	15	820	388	9999:1	−1	.....	287	46	115	15	130
Trinity clay	Sessums, Miss.	7.8	12	520	303	9999:1	77	142:1	380	61	112	7	119
Denham silt loam	Baton Rouge, La. †	5.9	20	978	475	9999:1	50	14:1	525	47	87	16	103
Ruston fine sandy loam	Calhoun, La.	6.4	20	953	358	9999:1	145	188:1	503	28	98	7	105
Yohola very fine sandy loam	Alexandria, La.	6.8	6	1443	397	260:1	125	4:1	522	51	90	14	104
Ruston fine sandy loam	Homer, La.	6.3	15	716	202	5999:1	138	192:1	340	15	55	32	87
Ruston fine sandy loam	DeRidder, La.	6.0	6	612	505	4699:1	238	195:1	743	22	40	30	70
Memphis silt loam	Gurley, La.	5.8	8	254	71	10:1	409	3332:1	480	42	7	18	25

* The pH was determined colorimetrically using Hellige color discs.

† The Louisiana soils had 4 per cent potash applied in the field in addition to the nitrogen and the nitrogen and phosphorus treatments.

‡ Replications.

of seed cotton of 448 pounds and 28 pounds respectively. In both the field and the laboratory very large increases were obtained from nitrogen alone and very small increases from phosphorus.

Ruston fine sandy loam.—This test was conducted for 4 years in the field. The increases in seed cotton for nitrogen and phosphorus were 397 pounds and 174 pounds respectively; the increase in CO_2 indicates increases of 328 pounds

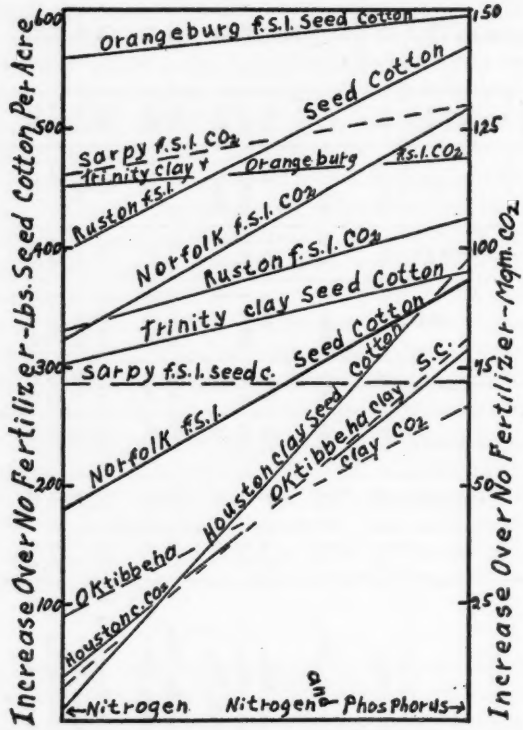

FIG. 1. RESPONSE OF COTTON AND SOIL MICROÖRGANISMS TO NITROGEN AND TO NITROGEN AND PHOSPHORUS—MISSISSIPPI SOILS

Scale—1 mgm. CO_2 = 4 pounds of seed cotton

and 92 pounds respectively. These differences are considered to be within the experimental error of the field results.

Norfolk fine sandy loam.—The field test was conducted 3 years. The increase obtained for nitrogen in one year which was extremely dry was 74 pounds per acre, whereas the average for the other 2 years was 231 pounds. The average increase for nitrogen for the 3 years was 179 pounds. The increase in CO_2 in the laboratory due to the addition of nitrogen indicates an increase in seed cotton of 320 pounds per acre. Phosphorus increased the yield of seed cotton

194 pounds; the increase in CO_2 obtained in the laboratory indicates an increase of 196 pounds of seed cotton for phosphorus.

Trinity clay.—The field data are reported for 3 years. The increases in seed cotton were 303 pounds and 77 pounds of seed cotton per acre for nitrogen and phosphorus respectively. The increases in CO_2 obtained indicate increases in yields of 448 pounds and 28 pounds of seed cotton per acre for nitrogen and phosphorus respectively.

Sarpy fine sandy loam.—The field data reported are for 5 years. Nitrogen made an increase in the yield of seed cotton of 288 pounds, whereas the increase in CO_2 produced indicates an increase in yield of seed cotton of 460 pounds, a difference of 172 pounds. This is the largest difference found in any of the tests, and it would be difficult to attribute all of the difference to field experimental error, but it is well to consider that the average increase in the seed cotton reported is derived from individual increases which vary from 61 to 740 pounds per acre. The addition of phosphorus did not increase the yield of seed cotton, whereas the increase in CO_2 obtained indicated an increase in seed cotton of 60 pounds. This difference is considered to be within the experimental error of the field work.

Houston clay.—This test was conducted for 3 years in the field. The nitrogen applied in the field was 8 per cent instead of 6 per cent as in the other tests. The same quantity of nitrogen was used on this soil in the laboratory as on the other soils. If the quantity of nitrogen used in the laboratory had been increased sufficiently to correspond with the amount applied in the field, the increase in CO_2 for nitrogen and phosphorus would have been somewhat larger. The lines representing increases in CO_2 and seed cotton would have almost coincided, indicating perfect agreement between the two methods.

Oktibbeha clay.—The field data are for 2 years. The increase for nitrogen and phosphorus together is 323 pounds; the increase in CO_2 indicates an increase in seed cotton of 268 pounds. The difference between the two methods (55 pounds) is considered to be within the experimental error of the field work. The increase per acre for nitrogen was 26 pounds of seed cotton, an average of 59 pounds on one year and −7 pounds on the other. The increase in CO_2 indicated an increase of 92 pounds of seed cotton for nitrogen. This difference is also considered to be within the experimental error of the field work.

The treatments in the Louisiana field tests which were used in comparison to the data obtained in the laboratory were:

Plot No. 1	600 lbs.	5–0–4
Plot No. 2	—	—
Plot No. 3	600 lbs.	5–8–4
Plot No. 4	—	—
Plot No. 5	—	—
Plot No. 6	—	0–0–0

Student odds were calculated on the assumption that the fertility of the soil between plots 1 and 6 is uniform. The soil for the laboratory work was col-

lected the middle of August; the laboratory determinations were made 3 months later. The data are reported in table 1, and those for four soil types are illustrated in figure 2.

Denham silt loam.—The field test was conducted for 5 years. The increase for phosphorus obtained in the field was 50 pounds per acre; the increase in CO_2 indicates an increase in yield for phosphorus of 64 pounds. The increase for nitrogen obtained in the field was 475 pounds, whereas the increase in CO_2

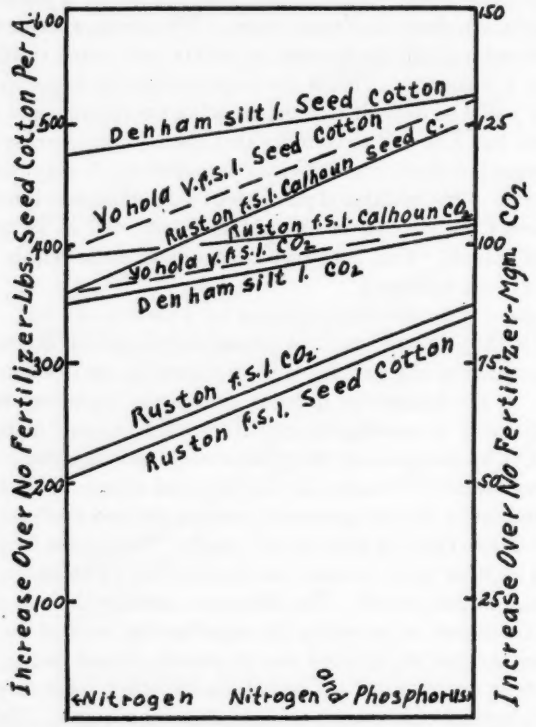

FIG 2. RESPONSE OF COTTON AND SOIL MICROÖRGANISMS TO NITROGEN AND TO NITROGEN AND PHOSPHORUS—LOUISIANA SOILS

indicated an increase of 348 pounds. The difference of 127 pounds per acre is very probably due to the control of boll weevils on this test, whereas on most of the other tests they were not controlled artificially.

Yohola very fine sandy loam.—This test ran for 2 years. The laboratory and the field method gave approximately the same response to nitrogen. The laboratory method gave an increase in CO_2 for phosphorus, which indicates an increase in seed cotton of 54 pounds per acre; 125 pounds with odds of only 4 to 1 were obtained in the field. The odds indicate that the increase obtained in the field was not due to the phosphorus.

Ruston fine sandy loam, Calhoun.—The field data are for 5 years. The increase in seed cotton for nitrogen obtained in the field was practically the same as that indicated by the increase in CO_2. The increase for phosphorus was 145 pounds of seed cotton per acre; the increase in CO_2 indicates an increase for phosphorus of only 28 pounds of seed cotton.

Ruston fine sandy loam.—The increases obtained in the field over a 4-year period were practically the same as those indicated by the increases in CO_2.

Ruston fine sandy loam from De Ridder, and Memphis silt loam.—The laboratory data indicate increases in seed cotton very much smaller than those obtained in the field. The differences are so great that the conclusion is reached that there is very little agreement in the data obtained by the two methods. The question naturally arises: "What is the lack of agreement due to?" It should

TABLE 2

The effects of air-drying soil for 24 hours and for 4 months and of the time of the year during which the soil is collected on the response of the soil microörganisms to nitrogen and to nitrogen and phosphorus

SOIL TYPE*	SOIL SAMPLE			MGM. CARBON DIOXIDE			
	Date taken	Date run	Condition	Yield, no fertilizer	Increase for		
					N	NP over N	NP
	1933	*1933*					
Oktibbeha clay	July	July	Air-dry	46	23	44	67
Oktibbeha clay	July	Nov. 3	Air-dry	47	2	11	13
Oktibbeha clay	Nov. 28	Dec. 1	Air-dry	39	27	14	41
Oktibbeha clay	Nov. 28	Dec. 1	Moist	34	13	12	25
Orangeburg fine sandy loam	Nov. 28	Nov. 30	Moist	20	128	2	130
Orangeburg fine sandy loam	Nov. 28	Nov. 30	Air-dry	22	125	4	129
Orangeburg fine sandy loam	July	July	Air-dry	32	112	7	119
Orangeburg fine sandy loam	July	Nov.	Air-dry	42	114	11	125

* All soils taken from Macon, Miss.

be borne in mind that 3 months elapsed between the time the soil samples were collected and the time the laboratory determinations were made.

The effect of storing air-dry soil from July until November on the CO_2 production.—In order to throw some light on the foregoing apparent disagreement between the two methods, Mississippi soils which were collected in July were used for laboratory determinations in November. The data are reported in table 2. Practically the same increases in CO_2 were obtained for fertilizers applied to the Orangeburg soil in July as in November, whereas there is no resemblance between the data for the July and November increases in CO_2 for the Oktibbeha soil.

Evidently air-drying for 4 months produced little change in the activity of the soil microörganisms of the Orangeburg soil, whereas much change took place in the activity of the soil microörganisms of the Oktibbeha soil.

The effect of air-drying soil for 24 hours on the production of CO_2.—Orangeburg and Oktibbeha soils were obtained from the fields in November. Determinations were made on fresh moist soil and on the soil after drying 24 hours. The data are reported in table 2. Air-drying did not materially affect the activity of the soil microörganisms in the Orangeburg soil as measured by CO_2 production but it increased markedly the activity of the soil microörganisms of the Oktibbeha soil.

The effect of the time of the year during which the soil is collected on the production of CO_2.—Soils were collected in November from several fields from which samples had been collected in July. The data for the Orangeburg and the Oktibbeha soils, reported in table 2, show that the CO_2 produced by the soil microörganisms of the Orangeburg soil was practically the same in November as in July, whereas there was a marked difference in the CO_2 produced by the microörganisms of the Oktibbeha soil when collected on the two dates. The laboratory data for all soils collected and run in July agreed with the field data, whereas the laboratory data for the November collected soils were very variable.

DISCUSSION

Soil microörganisms require approximately the same nutrients as do crop plants. The plants obtain energy from the sun, whereas soil microörganisms require the presence of an energy-supplying substance. The activity of the soil microörganisms depends upon the available nutrients and may be measured by determining the evolution of CO_2. The response of the soil microörganisms of a particular soil to nitrogen and to nitrogen plus phosphorus may be determined by measuring the increase in CO_2 produced by the addition of these fertilizers to mannite-treated soil. The results obtained in these experiments show that there is a high correlation between the response of soil microörganisms and cotton to nitrogen and to nitrogen plus phosphorus. Soil samples were obtained from 13 fields in which fertilizer experiments had been conducted for cotton, and the response of the soil microörganisms to nitrogen and phosphorus were obtained in the laboratory.

In 10 out of 13 cases the increase in CO_2 due to the addition of phosphorus plus nitrogen indicated increases in yields of seed cotton which came close enough to that actually obtained in the field to be within the range of the experimental error of the field data. In 9 out of 13 cases the increase in the CO_2 due to the addition of nitrogen came close enough to that actually obtained in the field to be within the range of experimental error of the field results. In 2 cases out of 13 the increase in yield of seed cotton from nitrogen alone was very much less than that indicated by the increase in the production of CO_2 in the laboratory.

The differences found between the two methods in the case of nitrogen are considered to be due to the irregularity in the distribution of those factors which favor cotton production.

In 2 cases out of 13 there was little correlation between the increases in CO_2 and seed cotton due to the addition of fertilizers. Further tests showed that this very probably was due to changes having taken place in the activity of the soil microörganisms during the lapse of 3 months between the collection of these soil samples and the laboratory determination.

The increase in CO_2 due to the addition of fertilizers to soils in July was in every case in direct proportion to the increases in seed cotton obtained in the field, whereas when the soil was collected in November in some cases there was almost no correlation between the field and the laboratory method.

Air-drying of soil collected in November was found to change markedly the activity of the soil microörganisms of some soils.

Carbon dioxide production on mannite-treated soil as a means of determining crop response to fertilizers has the following advantages over field tests:

1. Less than 30 hours is required to complete a test.
2. After the sample of soil reaches the laboratory, the actual time required to carry out the work is less than 3 hours.
3. The cost is sufficiently low to permit colleges to put in service departments to determine the fertilizer response of soils on which it is absolutely impossible to carry out field fertilizer experiments.

CONCLUSION

The production of CO_2 in soils to which mannite has been added under controlled laboratory conditions furnishes a basis for measuring the nitrogen and phosphorus requirements of soils for cotton. The nitrogen and phosphorus requirements of soils for other crops may be determined by this method as soon as the laboratory data have been properly correlated with sufficient field data.

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THE FACTORS WHICH INFLUENCE THE USE OF THE CONDUCTIVITY OF SOIL SUSPENSIONS AS A MEASURE OF FERTILITY

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The most fruitful application of conductivity measurements to the study of the soil has so far undoubtedly been the determination of total salts in saline deposits. As far back as 1897 Whitney and Means (22) evolved a quick electrolytic method for the determination of total salts in soils, which was further elaborated and improved upon by Briggs (3), Cameron and Briggs (4), Davis and Bryan (8), and others, until today the portable Wheatstone bridge has become an indispensable instrument to the soil surveyor engaged in the mapping of saline soils for purposes of reclamation or land utilization.

Atkins (1), however, was among the first to suggest conductivity as a measure of soil fertility. He showed that the conductivity of aqueous soil suspensions increased with time of extraction, tending towards a maximum value. Although some soils reached this maximum in a few hours, others continued to increase even after 10 to 14 days of continued extraction. CO_2, bacterial activity, and the solution of the soil material itself were suggested as factors influencing this change. He states: "A high electrical conductivity in the extract may only indicate the presence of excess salts and does not necessarily indicate a good soil. It seems however that a rapid increase as extraction is prolonged indicates increased solubility partly through bacterial action and may be considered as a useful indication of fertility. A low conductivity, which remains low on continuous extraction, denotes a soil so insoluble as to be infertile." Davis (7) confirmed Atkins' results.

Sen (18), employing a more standardized method of determination, e.g., excluding atmospheric CO_2 and using a constant temperature and a soil-water ratio of 1:5, found that the conductivity increase after 8 to 10 days bears a close relation to the fertility of the soil as checked by crop yield and crop growth. Fertile soils invariably showed large conductivity increases, infertile ones, slight or no increases. He states that of two soils practically identical in chemical composition but differing widely as regards crop response, the fertile one showed the highest conductivity increase, and concludes that "conductivity measurements are capable of accounting for failure to grow crops where chemical analysis yields no indication."

[1] The authors wish to express their thanks to Mr. A. J. Pugh, New Jersey Agricultural Experiment Station, for his interest and criticism.

Sen and Wright (20) applied the foregoing method to the study of soil samples taken from the Rothamsted fertility plots over a long period of years. Choosing the conductivity increase over a period of 7 days—"the 7 days' increase"—as an arbitrary maximum for comparison, they came to the following conclusions: On prolonged storage the initial conductivity is not markedly increased, but the 7 days' increase rises rapidly in a few months to a constant maximum value.

Manurial treatment influences both the initial conductivity and the 7 days' increase, and there exists a high positive correlation (0.859) between 7 days' increase of stored samples for various years and the crop yields for those years. If the time factor is eliminated, however, by calculation of a partial correlation, the value found is insignificant (+.061). When soil in a low state of fertility is allowed to run wild it shows an increase both in initial conductivity and 7 days' increase, which is in accord with normal cropping experience.

Sen (19) further studied the influence of cultivation, manuring, cropping, and meteorological variations on the cropped and uncropped Rothamsted plots. Although no seasonal change in unmanured plots of low fertility is evident, it is extremely marked in soils under permanent grass. To correlate 7 days' increase with fertility, measurements must be carried out when soil is in normal equilibrium, i.e., not shortly after the application of manures or the plowing in of stubble. A large 7 days' increase will then indicate that the soil is favorable to biological activities and therefore to the rapid liberation of plant food. Such a soil may therefore be expected to have a higher inherent fertility than one which has a smaller 7 days' increase.

Benade (2) has contributed a very interesting series of observations on the factors which influence conductivity increases in soils. The most important among these are (*a*) CO_2 absorption, (*b*) bacterial activity, (*c*) solution of the soil material, the quantitative contribution of each of which to the total increase was measured. As these results will be discussed in greater detail later, they will not be further elaborated here.

Judging from the evidence in hand, there would therefore appear to exist a general relation between conductivity increase in soils and crop response. The fundamental reasons for such a correlation are, however, as obscure as they are surprising, and the present paper is a further inquiry into the validity of these apparent relationships.

METHOD OF DETERMINING CONDUCTIVITY

Conductivity measurements were carried out by means of a Leeds and Northrup slide wire instrument, oscillator, and telephone, using a dip cell (cell constant = 1.04), conductivity water ($C = 15 \times 10^{-8}$), and a soil-water ratio of 1:5. The results are expressed as $C \times 10^{-6}$. The determinations were carried out in much the same way as suggested by Sen and Wright (20): 40 gm. of 2-mm. air-dry soil was placed in a resistant bottle, 200 cc. conductivity water added direct from fused silica receiver of conductivity water apparatus.

The suspension was agitated by an electrical stirrer, with the dip cell in position and in a current of CO_2-free air, the whole being carried out in a thermostat at 25°C. Measurements were taken every few minutes until the conductivity remained constant for 10 to 15 minutes. This value was the initial specific conductivity at 25°C. The suspension was left in the thermostat for 7 days, and the conductivity was again determined. Immediately before each determination the stirring was stopped for 100 seconds, in which time both the coarse and fine sand had dropped below the level of the dip cell, which was always immersed to a constant depth with respect to the surface of the liquid. The reason for this procedure will become clear from the discussion later.

The method of sampling is another very important item in measurements of this kind and can lead to serious variations in the same soil. This matter was given particular attention in these experiments, and no samples were used as duplicates or blanks until sampling could be carried out in such a way as to give the same initial conductivity.

EXPERIMENTAL RESULTS

The factors which influence conductivity fluctuations in soil suspensions can be grouped under the following heads: (*a*) adsorption of CO_2 from the atmosphere; (*b*) the action of microorganisms; (*c*) change in the degree of dispersion of the solid phase. Benade makes reference to these three, but there is also a fourth factor, (*d*) the formation of simple electrolytes as the result of solution of easily soluble salts, and the formation of colloidal electrolytes by hydrolysis of the colloidal complex.

To obtain information on the value for the initial specific conductivity, the following experiment was conducted.

It is a well-known observation that when soil is placed in water, the specific conductivity increases rapidly, a state of temporary equilibrium representing the solution of easily soluble salts being reached within from 15 minutes to somewhat over an hour, depending on the soil texture and the method of agitation used. After this point the conductivity remains practically constant, increasing relatively slowly with continued extraction, as a result, as will be seen later, of bacterial activity and hydrolytic changes in the soil complex. The first apparent maximum is a very well-defined point for all soils and is called the "initial conductivity." Thus:

Time.....	2 min.	5 min.	10 min.	19 min.	23 min.	28 min.	38 min.	24 hrs.	7 days
$C \times 10^{-6}$.....	67.0	73.9	120.4	185.6	199.8	203.6 ("Initial conductivity")	203.6	209.0	215.0

"Seven days increase" = Conductivity attained in 7 days, initial conductivity.
$= 215 - 203.6 = 11.4 \times 10^{-6}$

The action of Microörganisms

Any microbial activity in a soil completely immersed in water, as in the "7 days' increase" determination, must of necessity be greatly influenced by the artificial environmental conditions. If an adequate food supply is assumed, the aerobic organisms would be active from the start until such time as the high CO_2 concentration and consequent reduction in oxygen tension would cause them to be displaced first by facultative and finally by obligate anaerobes. Aerobic activity is hardly likely to last more than a few days under these conditions. On the other hand, it is well known that anaerobic forms require a considerable period of incubation for maximum development—up to 11 days under favorable circumstances. The strong presumption therefore exists that the initial aerobic activity is the only microbial contribution to be reckoned with and that the latter portion of the 7 days incubation period must be one of almost complete microbial inactivity. Evidence in support of this view is presented in the following.

If these arguments are correct, one must conclude that the CO_2 concentration of the liquid phase as influenced by the aerobic organisms is the limiting factor in microörganic activity, for only in extremely exceptional circumstances will a soil material be found so devoid of nutrients as to make this a limiting factor in an experiment of this kind. As the soil:water ratio in these determinations is constant (1:5), the feebler microbial activity in a poor soil will proceed for a longer time than that in a fertile one. Both will cease, however, when the same maximum CO_2 concentration has been reached.

The conductivity increase due to microbial action can therefore bear no relation whatsoever to the microörganic activity of the soil in its natural condition. The microörganisms under these conditions merely act as agents to produce a certain more or less constant CO_2 concentration, the whole process being analogous to shaking up a soil with water containing a fixed amount of CO_2, a method employed at various times in different parts of the world for determining available plant food.

If this is true, the increase due to organisms should bear a nearly constant ratio to the total increase whatever the nature of the soil. Soils so unweathered as to be entirely devoid of nutrients or those containing toxic elements, as for example excess of soluble salts, will be exceptions. In a series of quantitative studies on soil sterilized (with CS_2) and unsterilized, Benade (2) showed that the total increase is the resultant of microbial action and a solution effect on the soil body itself. His figures recalculated to show per cent increase due to bacteria are presented in table 1. From this it is clear that for these soils of different types the increases due to bacteria are practically constant, i.e., about 47 per cent of the total. For the South African soils examined it amounted to 50 per cent.

In order to test these points further, the following procedure was followed: Eight 40-gm. 2-mm. samples were taken from the same soil in such a way that their initial conductivities were identical, and the dry soil was placed in

resistant flasks and plugged loosely with cotton wool. Four of these were sterilized at 230°C. and 9 atmospheres pressure for 3 hours. To each of the eight flasks, 200 cc. freshly boiled and cooled conductivity water ($C = 16 \times 10^{-6}$) was added by means of a sterilized pipette, the same precaution against infection being taken as is normal in bacteriological work. The flasks were immediately stoppered, shaken, and placed in a thermostat at 25°C. When equilibrium had been attained (after 48 minutes determined by preliminary experiments) one sterile flask and one non-sterile flask were opened and the conductivities determined. This represented the initial conductivities for the purpose of correcting for any change in conductivity caused by the process of sterilization. After 2, 5, and 7 days this procedure was repeated. Results are presented in table 2 and graphically in figure 1.

It might be mentioned here that the procedure was repeated on the same soil on three different occasions, giving practically identical results, indicating that the sterilization and method of experimentation had been refined to the required degree of accuracy.

TABLE 1

Microörganisms and conductivity

SOIL TYPE	28 DAYS CONDUCTIVITY INCREASE		INCREASE DUE TO ORGANISMS	PER CENT OF TOTAL
	Sterile	Non-sterile		
	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	
Sandy soil (1.2 per cent humus).....	42.9	91.7	48.8	53
Drift sand (1.34 per cent humus).....	66.3	121.4	55.1	45
Clay soil (2.67 per cent humus).....	270.8	479.8	209.0	44

The results show that: (*a*) Microörganic activity practically ceases between the third and fourth day of incubation; (*b*) Further increases are due to hydrolytic and solution effects on the soil material; (*c*) The pH increases to nearly the same extent during incubation both in sterile and non-sterile soil. Benade, who found a similar pH increase, ascribed it to reduction processes under anaerobic conditions and the consequent production of NH_3. A more likely reason, however, is the hydrolysis of the complex, the dissociation of adsorbed bases, and the consequent increase of OH ions. In the presence of CO_2 this effect would probably be enhanced as the result of formation of bicarbonates. The point will, however, be discussed in greater detail later.

CONDUCTIVITY CHANGES DUE TO DEGREE OF DISPERSION OF THE SOLID PHASE

With regard to the influence of the soil particles themselves on the conductivity of a suspension, it has been pointed out before that the time taken for the attainment of initial equilibrium ("initial conductivity"), though usually greater for clayey than for sandy soils, would obviously depend on the state of aggregation of the soil particles.

Whitney and Means (22) many years back reported an illuminating series of observations on this point. They added increasing quantities of pure sand to the same volume of solution and found that the resistance increased slowly

TABLE 2

Microörganisms and conductivity

TIME	STERILE		NON-STERILE		INCREASE DUE TO MICROBES	INCREASE DUE TO SOLUTION
	$C \times 10^{-6}$	pH	$C \times 10^{-6}$	pH	$C \times 10^{-6}$	$C \times 10^{-6}$
days						
0	164.2	5.55	143.2	5.38	....	....
2	178.2	5.59	169.1	5.43	11.9	14.0
5	182.0	6.08	184.4	5.76	23.0	17.8
7	183.5	6.14	185.8	6.23	23.3	19.3

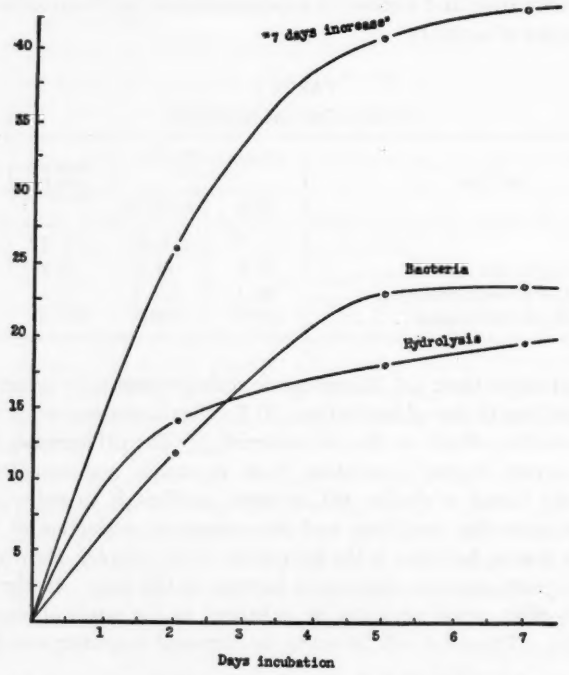

FIG. 1. CONTRIBUTING FACTORS IN "7 DAYS INCREASE"

up to the point of complete saturation and after that very suddenly, resulting into two straight lines intersecting at the point of complete saturation of the soil by water. Beyond this point air would begin to fill the pores and with decreasing moisture content the thickness of the films round the particles

would continuously decrease. The effect of this on ionic mobility would be analogous to a lengthening of the path between the electrodes. With soils of different texture, adjusted to the same salt and moisture content (below the point of complete saturation), the resistance increased with increasing surface area, i.e., with decreasing thickness of the moisture film. In the same way a soap solution had a higher specific conductivity than an equivalent amount of foam.

Haines (10) and Cashen (5), following up the work of the Bureau of Soils, have used conductivity measurements to study possible discontinuities in the soil-moisture curve below the point of complete saturation. Cashen points out that the net effect of the movement of ions, which are naturally more concentrated at the soil-water interface, is similar to the passage of an alternating current through a condenser resulting in a phase difference between the applied E. M. F. and the current flowing. His apparatus is designed to measure such capacity changes in a system decreasing in moisture content. Haines has pointed out, however, that drying has to be very slow in order to obviate differences in moisture content between different parts of the soil block. A drying process lasting over several days would introduce changes in the electrolyte content, both as the result of bacterial action and changes in the colloidal complex on the one hand, and a reduction in the moisture film on the other. The conductivity at any particular moisture content must therefore be the resultant of a series of opposing forces, on the one hand an increase in electrolyte content, as well as surface conductance effects tending to cause increased conductivity, and on the other a decrease in the thickness of the moisture film tending to decrease the conductivity.

Cashen appears to have looked upon the soil as a more or less inert aggregation of particles surrounded by films of constant electrolyte concentration, and has disregarded almost entirely any physico-chemical changes accompanying the process of desiccation. It is difficult to see how his figures can reflect true discontinuities in the soil-moisture curve with any degree of accuracy.

Above the point of complete saturation inert particles like sand will have little or no effect on ionic mobility, so that at a 1:5 soil-water ratio any such influence can be entirely disregarded. If the conductivity of a soil suspension is therefore determined by ionic mobility alone, it should be unaffected by the coarser particles, e.g., sand and fine sand. To test this point, different soil suspensions (1:5) were stirred at 25°C. (by means of an electric stirrer) until initial equilibrium was attained, the dip cell being in position at a fixed depth. At this point the stirring was stopped and the coarse and fine sand allowed to drop below the electrodes—under the given set of conditions constancy was obtained in 100 seconds—and the conductivity again measured. The suspension was then centrifuged for 45 minutes and the determination repeated (table 3).

From these results it would appear that the conductivity is increased as the

coarser particles are removed, first by sedimentation and then by centrifuging. The centrifuged material was a translucent sol and the only obvious explanation of the phenomenon is that the finest sol particles must act like ions and contribute to the conduction of the current, with mobilities not very far removed from that of the ions themselves. Although the coarser suspended material has no influence on the mobilities of the ions, they very definitely retard the movement of these complex ions, thus causing an increase in conductivity when the mechanical obstruction is removed.

Soils A and B, respectively a ferruginous and highly silicious clay, behaved somewhat differently on centrifuging. Here the total number of dispersed

TABLE 3

Influence of coarse particles on conductivity

STIRRING TIME	SOIL NUMBER							
	364	404	373	355	371	444	A	B
	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$	$C \times 10^{-6}$
minutes								
2	146.9	180.3	162.5	30.2	.....	142.0	112.7	93.0
5	149.7	184.9	165.2	.....	73.9	145.3	115.4	97.9
10	151.6	192.9	170.0	31.7	120.4	148.4	118.7	106.5
15	**152.2***	200.7	**170.2**	.....	160.0	150.2	129.0	114.7
20	152.2	208.7	170.2	32.8	190.0	151.4	122.5	122.7
30	152.2	221.5	170.2	33.6	**203.6**	152.9	124.9	**137.0**
35	152.2	**222.3**	170.2	34.7	203.6	.....	125.5	137.0
50	152.2	222.3	170.2	**35.4**	203.6	154.7	**126.9**	137.0
60	152.2	222.3	170.2	35.4	203.6	155.2	126.9	137.0
70	152.2	222.3	170.2	35.4	203.6	**155.8**	126.9	137.0
80	152.2	222.3	170.2	35.4	203.6	155.8	126.9	137.0
Sedimentation for 100 seconds...	163.5	225.0	184.4	36.5	218.0	162.1	134.2	145.0
Centrifuged 45 minutes.....	173.2	228.7	213.1	37.9	220.2	168.9	130.5	132.4
Per cent clay.....	.....	.....	10.9	13.0	19.0	22.0	50.0	50.0

* Figures in boldface type represent the "initial conductivity."

particles is large and some are obviously carried down by the coarser material, causing a decrease in conductivity on centrifuging. These results seem to be in agreement with those of McBain (11), who found in his work on soap solutions that if the fatty acid chain is increased until it attains a size incommensurate with molecular dispersion the particles formed have mobilities of the same order as that of ions.

A fairly close relation therefore appears to exist between conductivity, electrophoresis, and surface conductivity, and Pugh (16), in a discussion on electrokinetic potentials in the light of the work of Michaelis (14), McBain (11), Loeb (15), and in particular that of Mattson (12), presents a summary of these

views. In solution the colloidal micelle with its double layer can be considered in many respects similar to the molecule of an electrolyte. There is an analogous space differentiation between anionic and cationic components, but, although the ions in electrolytes distribute themselves nearly uniformly through the whole solution, in the case of the micelle, electrostatic effects cause the cations, which though free to move amongst themselves, to be arranged in the nature of a diffuse swarm around the complex anion. Under the influence of an electric field, anions and cations move in opposite directions, so that visible movement of the anionic micelle, which is known as cataphoresis in the case of electronegative colloids, can therefore be regarded as a limiting case of conduction in electrolytes.

The transition from a molecularly dispersed to a colloidally dispersed state is one of degree and represents a change from a condition where electrostatic attractions are infinitely small to one where they are highly marked, with an intermediate zone where particles show the properties of both extremes and mobilities approaching those of individual ions. Such particles would contribute to the conduction of a current and influence conductivity measurements. With increase in size and consequent reduction in mobility the bigger particles, although capable of cataphoretic movement, will obstruct the movement of the transitional micelles.

These arguments naturally apply to dilutions where the particles have comparatively free movement. If the number of particles is increased to a point where individual movement ceases, as in a gel or a block of damp soil, endosmotic effects become dominant and the cationic movement of the adsorbed ions manifests itself as surface conductance.

HYDROLYSIS OF THE COMPLEX

One of the outstanding properties of weak electrolytes is their tendency to hydrolyze, which is now generally recognized as due to the higher affinity of the H ion for the weak acid ion as compared with other cations. The reaction, which can be represented thus:

$$XM + H_2O \rightleftharpoons XM + H' + OH' \rightleftharpoons XH + M' + OH'$$

therefore gives rise to OH ions and cations, the solution tending to become alkaline.

The mineral silicates as well as the soil complex are salt-like substances consisting of an anionic and cationic component, which in water behaves much like weak electrolytes. Thus powdered feldspar when shaken up with water will yield cations and an increased pH, whereas analyses of weathered and unweathered rocks like granite show a considerable loss of cations in the weathered material. In fact this reaction is regarded as one of the most potent factors in the weathering of rocks and soils, and dealkalization as the first step in this process (20).

Although, because of the amphoteric nature of soil colloids, conductivity

measurements have little or no meaning in physico-chemical studies on them, they can be used as a relative measure of the total amount of basic material dissociated when a given soil is treated with a given amount of water.

In the absence of many soluble salts the action of water on soil material would be largely one of hydrolysis and increased dispersion. Drachev (9) has attempted to measure this hydrolysis by means of conductivity determinations assuming that Ostwald's equation for weakly associated binary electrolytes holds for soil colloidal micelles, i.e.

$$\frac{a^2}{(1-a)v} = K \text{ or } a = \sqrt{KV}$$

in the case of soils where dissociation is small (a = dissociated part of molecule, v = volume of solution). By plotting milligram equivalents electrolyte dissociated against dilution, he obtained a series of characteristic straight lines from which a solubility factor for different soil types could be deduced. There are, however, a number of discrepancies in Drachev's method of treatment. For example, he does not indicate how he reduces conductivities in solutions of mixed ions to milligram equivalents electrolyte, which on the face of it must entail certain assumptions and approximations. In the second place, for conductivity measurements applied in this way to have any meaning at all, they must be carried out on equivalent concentrations of colloid. Cziky (6) has pointed this out in comparisons of base exchange capacity, and it certainly applies with equal force here. To compare hydrolysis of a chernozem complex with that of a podzol, therefore, it is necessary to use equivalent quantities of colloid as regards base exchange capacity. The different solubilities found by Drachev may therefore either all have been equal or of an entirely different order, had the colloidal materials been used in equivalent concentrations. As has been pointed out, however, the validity of applying conductivity determinations in this way can be questioned on the grounds of both the amphoteric nature of the colloid and the influence of dispersion on conductivity.

In the following experiment the relation between dispersion and increase in conductivity was tested. Soils differing in pH and clay content were boiled with conductivity water (1:5) under a reflux condenser, thus excluding CO_2 and bacterial action, for various periods. At different periods the change in conductivity and dispersion was determined. From the results given in table 4, it will be seen that both the conductivity and the degree of dispersion increase with boiling. The rate of this increase differs from soil to soil, but as equivalent concentrations of complex were not taken, this does not reflect different degrees of hydrolysis of the complexes, but that of the whole soil body, thus including the diluting effect of the sand and coarser particles, as is normally the case in determining available plant food in the laboratory.

In most soils there is a rapid conductivity increase during the first few hours. After that, however, increases with time are comparatively slight (fig. 2). In a few instances soils like 371 and 367 were found which increased at a nearly

constant rate almost indefinitely, a difference which is by no means always reflected by ordinary chemical analysis.

If the degree of dispersion is plotted against conductivity increase (fig. 3), it would appear that conductivity increases in a fairly regular manner with increasing dispersion, in some cases actually resulting in a straight line, but it is somewhat more rapid than change in dispersion. Such a close relation is naturally to be expected, for with an increase in the number of finer particles an increased surface is exposed to the effects of hydrolysis. In some soils, however, though a limit is reached in dispersion, conductivity increases continue, showing the essentially independent nature of the two processes.

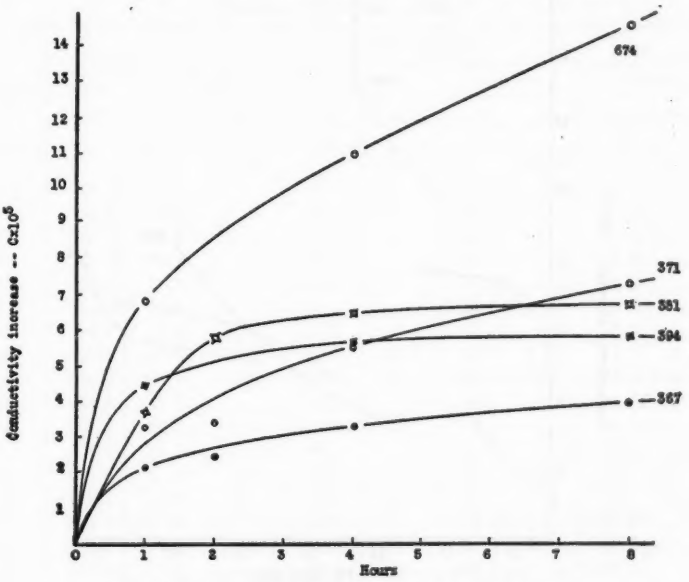

FIG. 2. CONDUCTIVITY INCREASE DUE TO HYDROLYSIS

The hydrolyzability of soil material is largely influenced by the nature of the complex, the amount and nature of the adsorbed base, and the pH. From the point of view of conductivity increases, the following three possibilities present themselves:

(*a*) In unsaturated soils of low pH the total amount of hydrolyzable metallic ions is small, the complex being nearly saturated with H ions. If such a complex were stable, the amount of hydrolysis and therefore conductivity increase would be negligible, as the H ion is the most actively adsorbed ion. As it happens, however, colloidal ferric silicate complexes at a pH below 5.4 become highly unstable (16), and solubility effects on the iron in the complex become noticeable. Any increases in conductivity in acid soil must therefore

be greatly influenced by the disintegration and solution of the soil complex itself.

(*b*) As the complex becomes more saturated with bases at higher pH values, it becomes highly stable, and in normal soils the predominant adsorbed bases are divalent Ca and Mg ions. Hydrolysis here would set free cations of importance in plant nutrition. The power of a soil to maintain a steady supply of such hydrolyzed material would depend on the percentage of colloidal matter, i.e., on the degree of weathering.

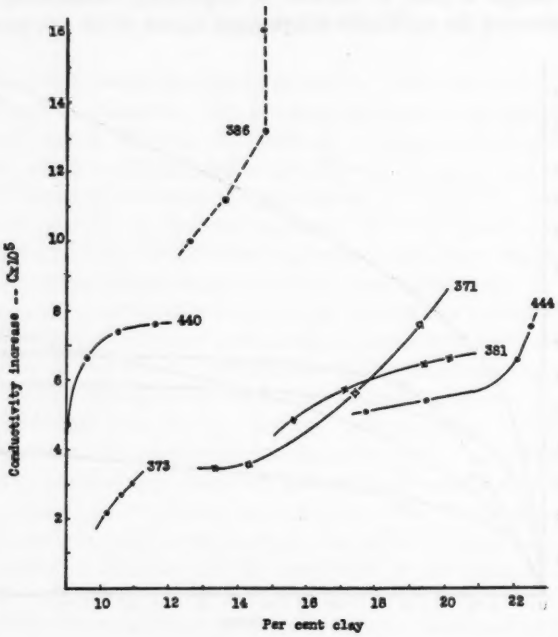

FIG. 3. RELATION BETWEEN DISPERSION AND CONDUCTIVITY INCREASE

(*c*) In alkaline soils where Na ions predominate, the effect of dispersion and hydrolysis would be enormous due to the hydration of the Na ion. In the presence of a large excess of soluble salts, this would naturally be prevented and under such circumstances it might be found that hardly any increases in conductivity would take place after initial equilibrium is attained. Such a state of affairs would therefore bear no relation whatever to bacterial activity, as was indicated by Sen. In a solonetz, where the Na complex is largely free from soluble sulfates and chlorides, the possibility exists that hydrolysis might be so rapid as almost to be complete in the time required for the establishment of equilibrium of easily soluble material. In such a case there would also be

no conductivity increases over long periods. In soil formation the latter process is known as solodification and can in time give rise to a degraded solonetz saturated with H ions.

CONDUCTIVITY AND FERTILITY

It has been shown that conductivity measurements can be used to determine the amount of readily soluble electrolyte in a soil suspension (1:5) at any moment, as well as the changes in electrolyte content resulting from bacterial

TABLE 4

Hydrolysis of soil due to boiling

SOIL NUMBER	INITIAL CONDUCTIVITY $C \times 10^{-6}$	TIME OF BOILING							
		1 hour		2 hours		4 hours		8 hours	
		$\overset{\Delta}{C} \times 10^{-6}$*	Clay	$\overset{\Delta}{C} \times 10^{-6}$	Clay	$\overset{\Delta}{C} \times 10^{-6}$	Clay	$\overset{\Delta}{C} \times 10^{-6}$	Clay
			per cent		*per cent*		*per cent*		*per cent*
404	13.39	16.0	....	20.9	....	27.0	.....	35.1	.....
382	30.3	22.5	....	28.8	....	39.7	.....	57.1	.....
405	31.91	30.9	....	36.8	....	45.9	.....	52.2	.....
406	42.21	18.4	....	23.8	....	35.7	.....	57.9	.....
388	69.00	47.2	....	56.5	....	74.8	.....	94.2	.....
367	80.3	21.9	....	24.8	....	32.5	.....	40.5	.....
361	84.7	21.0	....	41.0	....	47.6	.....	72.2	.....
444	119.8	49.3	17.6	51.7	19.3	63.5	21.9	72.8	22.2
386	134.3	97.1	12.5	109.5	13.5	128.2	14.58	156.2	14.58
364	138.4	34.5	....	35.8	....	48.7	.....	56.01	.....
394	141.5	43.1	....	47.4	....	55.2	.....	58.5	.....
373	164.9	21.2	10.28	20.0	....	26.4	10.6	29.5	10.94
440	185.8	47.6	9.1	64.0	9.6	71.6	10.5	76.1	11.5
371	211.3	32.6	13.2	34.0	14.2	53.7	17.3	73.1	19.0
409	213.7	37.5	....	54.3	....	66.8	.....	81.87	.....
381	255.3	36.4	15.5	54.8	17.0	63.4	20.0	67.0	.....
674	265.0	67.7	....	77.0	....	109.1	.....	146.8	.....
355	291.8	27.7	11.7	39.5	11.7	.....	12.4	49.04	13.0
673	1,073.0	52.2	....	....	....	130.9	.....	186.0	.....

* $\Delta.C \times 10^{-6}$ is difference between conductivity and "initial conductivity."

activity, hydrolysis, and dispersion. To correlate such measurements with crop response is to assume that soil fertility, i.e., the power of a soil to produce crops, is not only primarily a matter of electrolyte content but also one independent of the nature of the electrolyte. It is, however, common knowledge that insofar as crop response can be correlated with soil conditions alone, the main factors are the availability of specific mineral nutrients, which in their turn depend on organic matter content, microbial activity, and physical and moisture conditions.

Proof has further been advanced that conductivity increases, measured in

this way, bear scant relation to the microbial activity of the soil, the factors which advance or retard it, and therefore to the important process of nitrification. They do, however, serve as a rough measure of the hydrolyzability of soil material, i.e., the ability of the soil to split off adsorbed bases whether such bases have a plant nutritional value or not. This can, however, be far more efficiently determined by boiling a soil with water in the absence of CO_2 than by the "7 days' increase" method, and from table 5, where these two determinations are compared, it is obvious that no relation whatever exists between them. Although one would naturally hesitate to correlate crop yields with these values, this has been done here for comparative purposes. Since most of

TABLE 5

Relation between "7 days increase," hydrolysis, and crop yield

SOIL NUMBER	7 DAYS INCREASE $C \times 10^{-4}$	8 HOURS BOILING INCREASE $C \times 10^{-4}$	RELATIVE CROP YIELD	REMARKS
404	27.5	35.0	...	
364	19.0	36.0	480	Strong N, no P response
367	6.3	40.5	580	N P response, no K
355	14.6	49.0	589	Weak P and K, strong N response
405	43.9	52.2	...	
382	53.0	57.1	...	
406	9.6	57.9	...	
394	50.7	58.5	...	
381	42.3	67.0	685	P and strong K response
361	13.8	72.2	906	Strong N P, no K response
371	9.0	73.1	...	
409	13.0	81.8	...	
388	64.9	94.2	800	Strong K P response
674	94.0	148.2	...	
386	32.9	156.2	...	
673	226.0	186.0	...	

the soils are from the check plots of wheat manurial trials, both their chemical composition and their nutrient deficiencies are known.

In most of them too, climate, drainage condition, organic matter content, and texture are very similar indeed, so that there is some justification for this comparison. It will be noticed from table 5 that crop yields increase with increasing hydrolysis as measured by 8 hours boiling in water, but bear no relation whatever to the 7 days' increase. This brings out the further point that in soils where conditions are essentially the same, and where crop differences are largely due to mineral deficiencies, correlations of the kind obtained by Sen on the Rothamsted plots, stretching over many years, can be expected. Its application in a similar way to soils in general, however, is entirely unwarranted.

Although conductivity measurements are invaluable in the study and mapping of saline soils, their application to soil fertility studies on the one hand, and to the nature of the colloidal complex on the other, is undoubtedly subject to very considerable limitations.

SUMMARY

Conductivity changes in soil suspensions in the absence of atmospheric CO_2 are caused by (*a*) microörganic activity, (*b*) changes in degree of dispersion of the solid phase, (*c*) dissociation of electrolytes, resulting from solution of easily soluble salts and from hydrolysis of the colloidal complex.

Microörganic activity in "7 days' increase" is chiefly aerobic and ceases after a few days of incubation. This contribution to conductivity increase is arbitrary and analogous to shaking up a soil with water containing CO_2. It bears no relation to the true microörganic activity of the soil.

During incubation, pH increases as a result of hydrolysis of adsorbed bases and possibly some solution due to the presence of CO_2, with formation of bicarbonates.

Cataphoresis and surface adsorption are limiting cases of conduction in electrolytes.

The finer sol particles contribute to the conduction of a current, and the degree of dispersion of the soil is therefore an important factor in conductivity determinations.

Hydrolyzability of the soil complex is a function of the nature of the complex, the nature and quantity of adsorbed ions, and the pH.

In physicochemical comparisons of the colloids in different soil types, equivalent quantities of colloid as regards base exchange capacity must be used. The amphoteric nature of soil colloids sets a serious limit to the usefulness of such measurements.

The relationships between fertility, "7 days' increase," and hydrolysis are discussed.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XV. THE DEGRADATION AND THE REGENERATION OF THE SOIL COMPLEX[1]

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When the soil complex reacts with the common, easily displaceable ions the process is reversible and the complex is left intact, retaining its identity, its isoelectric point, and its exchange capacity. When other ions which form very slightly dissociated combinations react with the soil complex the latter changes its character and behavior. Such strongly associated ions become a part of the colloidal ion complex and modify its properties by changing the strength and magnitude of the acidic and basic residues. Thus when phosphate, silicate, or humate ions react with a soil colloid (especially one having a low silica/sesquioxide ratio) there is an increase in the strength of the acidic and a decrease in the basic residue, a lowering of the isoelectric point, and an increase in the cation exchange capacity. Conversely if aluminum or a similar ion is precipitated with a soil colloid (especially one having a high silica/sesquioxide ratio) there is a decrease in the strength of the acidic and an increase in the basic residue, an elevation of the isoelectric point, and a decrease in the cation exchange capacity. These facts were brought out in some of the preceding chapters of this series (3, V, VI), but since then a more detailed study of this phenomenon has been made, the results of which will be here discussed.

THE CHEMICAL NATURE OF THE EXCHANGE COMPLEX

The soil complex consists of weak, mostly insoluble or slightly soluble polyvalent acids and bases. To illustrate the reactions of compounds of such acids and bases we shall again make use of the following scheme:

Assume a tribasic acid $H_IH_{II}H_{III}A$ and a base $BOH_{III}OH_{II}OH_I$. The activities of the three H ions are

$$H_I > H_{II} > H_{III}$$

and that of the OH ions

$$OH_I > OH_{II} > OH_{III}$$

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The most simple combinations between the acid and the base would result when equivalent proportions react thus:

$$H_I\,H_{II}\,H_{III}\,A + BOH_{III}\,OH_{II}\,OH_I \leftrightarrows \qquad (A)$$

$$H_{II}\,H_{III}\,A \cdot BOH_{III}\,OH_{II} + H_2O \leftrightarrows \qquad (B)$$

$$H_{III}\,A : BOH_{III} + H_2O \leftrightarrows \qquad (C)$$

$$A : B + H_2O \qquad (D)$$

The extent to which the mutual combination or neutralization will take place will depend upon the ionization of the acid, of the base, and of the salt, for although the latter is insoluble it ionizes to some extent and this will prevent a complete "neutralization." The compound will, in other words, remain more or less hydrolyzed. If the product

$$[H_{III}]\,[OH_{III}] < K_w$$

and if the ionization

$$A : B \rightarrow A^- : B^+$$

proceeds to a certain slight extent the reaction would stop at (*C*) and we would have the compound

$$HA : BOH \qquad (E)$$

In other than equivalent proportions of acid and base the reaction would be more complex and give rise to compounds of the type

$$\begin{matrix} & & H_2A \\ & \diagdown & \\ & BOH & \\ & \diagup & \\ H_2A & & \end{matrix} \qquad (F)$$

and

$$\begin{matrix} & & B(OH)_2 \\ & \diagup & \\ HA & & \\ & \diagdown & \\ & & B(OH)_2 \end{matrix} \qquad (G)$$

Furthermore if both the acid and the base are themselves insoluble they might enter in any proportion into the make up of the colloidal micelle, which contains thousands or millions of molecules.

The isoelectric point of the various compounds will be governed by the relative strength of the acid and basic residue. The isoelectric point of compound (*F*) will be lower than that of compound (*E*) and will be highest in the case of compound (*G*). These compounds will react amphoterically: with

bases at pH values above their isoelectric point and with acids below this point. If the isoelectric point is lower than pH 7.0, that is, if the acid residue is the strongest, as is usually the case in soil colloids, the complex will adsorb and exchange cations from neutral salt solutions. The cation exchange capacity will obviously be greatest in (*F*) and smallest in (*G*) (per gram colloid). The ultimate pH will be lowest in (*F*) and highest in (*G*).

EXCHANGE REACTIONS

We shall now see how we might expect these compounds to react with different electrolytes. These amphoteric compounds are themselves salts whose residual H and OH ions are attached to spatially separate groups whose union depends upon the pH of the medium. Their behavior will therefore be different from the behavior of ampholytes whose acidic and basic characters reside in a single group such as the amphoteric hydroxides. It is obvious that the union, i.e., the number of bonds, between A and B will be at a maximum in the absence of stronger acids and bases, that is, at the ultimate pH or near the isoelectric point. If a strong base is added to a compound of type (*E*) the H ion will first be displaced thus:

$$NaOH + HA : BOH \rightarrow NaA : BOH + H_2O$$

But the reaction will not stop here, for sooner or later as the pH is increased the compound will undergo hydrolytic cleavage, resulting in the following change:

$$NaOH + NaA : BOH \rightarrow Na_2A \cdot B(OH)_2$$

and finally at a sufficiently high alkalinity:

$$NaOH + Na_2A \cdot B(OH)_2 \rightarrow Na_3A + B(OH)_3$$

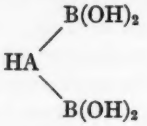
This hydrolytic reaction, which undoubtedly takes place in the soil, is very important, for it shows that the amount of base which a soil will bind is greater than the number of equivalents of displaceable hydrogen actually present in the unsaturated soil. It has previously been shown (3, V) that the cation exchange capacity of a soil colloid can be built up permanently by treating the material with strong alkali. The process undoubtedly consists in a hydrolytic cleavage of the amphoteric complex, that is, in an unlocking of the bonds between the acidoid and basoid groups. How much of the hydrogen displaceable at pH 7.0 by the neutral salt treatment actually exists as such in the unsaturated soil is difficult to say. It is certain that the displaceable hydrogen does not correspond to the amounts of adsorbed bases at higher pH values.

A similar hydrolytic cleavage results, of course, when an amphoteric compound of this type is treated with strong acids.

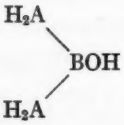
THE ISOELECTRIC DECOMPOSITION OR DEGRADATION OF THE COMPLEX

The presence of strong acids or bases leads to a suppression of the ionization of the corresponding group in the amphoteric complex whereas the ionization

of the opposite group is greatly increased. *Now since the ionized (charged) group is more dispersible and soluble than the unionized (uncharged) group it follows that the colloidal complex will, through a hydrolytic cleavage, lose some of the former and become enriched in the latter group.* At pH values above the isoelectric point the acid group will be ionized and will to some extent pass into solution. If the soluble products are removed by leaching, as under natural conditions in the soil, the process is irreversible. The complex will become richer in the basic group, and this will elevate the isoelectric point until it approaches the prevailing pH when the complex will again be stable. Instead of the original compound HA : BOH we shall end up with a more basic one, as for example



At pH values below the isoelectric point the basic group will be ionized and split off, leaving a complex which possesses a stronger acid residue, a lower isoelectric point, and a greater stability at the lowered pH as indicated by the following formula:



This process, by which the activated, ionized group continually tends to split off from the complex was laid as a basis for the theory of isoelectric weathering (3, IX) and is represented in nature by podzolization as one extreme and laterization as the other.

ISOELECTRIC SYNTHESIS OR REGENERATION OF THE COMPLEX

A simple rule of the mass law is that when two ions which together constitute an insoluble compound are mixed, then that compound will be formed. This rule might be applied to colloids as follows:

When an ion which, in combination with a colloid, forms an isoelectric complex is added to the colloid then that complex will be formed in preference to all other combinations, and the displaceable ions already in combination with the colloid will be effectually displaced. An ion of this type can only be displaced by other ions of a similar type or by hydrolytic action at pH values far above or below the isoelectric point. If the colloid is originally an amphoteric colloid then its isoelectric pH will be deflected: upward if the ion be a cation and downward if it be an anion.

The isoelectric complex is least ionized and represents, therefore, the most stable condition. The complex will, therefore, strive to assume this condition. This can be accomplished not only by the loss through a hydrolytic cleavage of

the ionized active group as already outlined but also by the neutralization of the charge through the association of a non-dissociable ion. In contradistinction to the term "isoelectric decomposition" this process might be termed "isoelectric synthesis." It constitutes the basis for the regeneration of soils.

Before we present the experimental work dealing with this problem we shall devote a few additional lines to a theoretical treatment of the reactions envolved.

Suppose the pH x of the medium be such that a compound of the acid H_3A and base $B(OH)_3$ would be isoelectric in equivalent proportions thus

$$HA : BOH$$

But assume now that the actual composition of the compound be

$$\begin{matrix} & & B(OH)_2 \\ & \diagup & \\ HA & & \\ & \diagdown & \\ & & B(OH)_2 \end{matrix}$$

the isoelectric point of which will be higher than x. The compound will therefor exist in a partly combined condition with acid anions, e.g., Cl, thus:

$$\begin{matrix} & & BOHCl \\ & \diagup & \\ HA & & \\ & \diagdown & \\ & & BOHCl \end{matrix}$$

The compound would be positively charged through the dissociation of the Cl ions, but this charge would be neutralized and the compound rendered isoelectric in the presence of sufficient quantity of a weak acid of the type H_3A, which forms a nondissociated compound with B according to the equation

$$\begin{matrix} & BOHCl \\ HA & \\ & BOHCl \end{matrix} + H_3A \rightarrow 2\ HA{:}BOH + 2\ HCl$$

If we assume the composition of the original compound to be

$$\begin{matrix} H_2A & & \\ & \diagdown & \\ & & BOH \\ & \diagup & \\ H_2A & & \end{matrix}$$

then its isoelectric point will be lower than x and the compound will exist in a partly saturated condition with metal cations, e.g., Na, thus

$$\begin{matrix} NaHA & & \\ & \diagdown & \\ & & BOH \\ & \diagup & \\ NaHA & & \end{matrix}$$

This compound, which will be negatively charged, will be rendered isoelectric in the presence of a sufficient quantity of a weak base of the type $B(OH)_3$ according to the following equation:

$$\left.\begin{matrix} NaHA \\ \\ NaHA \end{matrix}\right\rangle BOH + B(OH)_3 \rightarrow 2\ HA{:}BOH + 2\ NaOH$$

In both cases we obtain a compound of the type HA : BOH, which on assumption is isoelectric at pH x. In the first case the isoelectric point is lowered and the cation exchange capacity is increased, whereas in the second case the effect is the opposite. The power of the complex to bind anions is decreased in the first case and increased in the second.

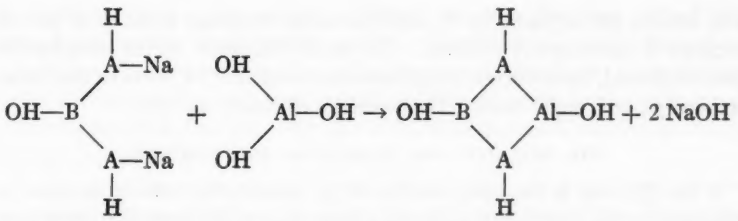
THE ALUMINATED SOIL COMPLEX

The last type of reaction takes place when a soil is isoelectrically precipitated with an aluminum salt. In table 134 the cation exchange capacity of the original and that of the aluminated Sharkey and Sassafras soil colloids are compared. The isoelectric point was determined exactly as in the case of bentonite as shown in table 58 A (3, IV). With 1.5 millimol $AlCl_3$ per gram Na-saturated colloid the Sharkey was isoelectric at pH 6.0 and the Sassafras at pH 6.8.

The isoelectric precipitation in bulk was then brought about by mixing 1 liter containing 1 gm. Na-saturated colloid plus the required amount of NaOH with 1 liter containing 1.5 millimol $AlCl_3$. The precipitate was then placed on the filter and the cation exchange capacity determined by the neutral Ba-acetate method as in the case of the original colloid. The isoelectric point of the original Sassafras colloid in HCl was about pH 4.3. In the case of the Sharkey colloid this value cannot be determined cataphoretically by our cell because of the evolution of gas at the electrodes at the low pH required, but judging by the pH of exchange neutrality of this colloid in a NaCl solution the isoelectric point would be about pH 3.0.

The 1.5 millimol $Al(OH)_3$ tied up and inactivated more than 60 per cent of the exchange valences active at a pH of 7.0. The earlier experiments with bentonite yielded the same results. The considerably weaker base $Fe(OH)_3$ produced a much smaller effect. It is obvious that a still stronger base which yet forms a practically nondissociated compound with the acid group of the colloid, and would therefore not be displaceable by the neutral salt cations, would still further reduce the cation exchange capacity. Thus Anderson and Byers (1) found that ferrous hydroxide in certain cases entirely suppressed the ammonia adsorption by soil colloids.

The following equation will serve to illustrate why the isoelectric point is raised and the cation exchange capacity is reduced by the reaction:



A and B represent the acid and basic groups in the original colloid. It will be noted that the basic residue has been increased and that the acid residue has been decreased by the reaction. Both of the aluminated colloids were isoelectric below pH 7.0 and retain, therefore, some power to adsorb and exchange cations at this point.

It is interesting to speculate about the action of the fairly strong base ferrous hydroxide in a soil under reducing conditions, below the ground water level. The ferrous ion is here formed by the reduction of the very weak base, ferric

TABLE 134

The cation exchange capacity of the original and the aluminated Sharkey and Sassafras soil colloids

Milliequivalents per gram

COLLOID	ISOELECTRIC POINT		EXCHANGE CAPACITY		DECREASE IN EXCHANGE CAPACITY
	Original	Aluminated	Original	Aluminated	
	pH	*pH*	*m.e.*	*m.e.*	*per cent*
Sharkey	3.0 ?	6.0	0.783	0.267	66.0
Sassafras	4.3	6.8	0.326	0.125	60.7

hydroxide. A weak base changes to a strong base whose cation powerfully displaces the exchangeable cations of the common still stronger bases. This fact readily explains the high pH common in such soils even in the colder regions of heavy rainfall. If the displaced bases are leached out and if the soil is then drained, the iron will be oxidized and largely hydrolyzed into free $Fe(OH)_3$ thus leaving an unsaturated acid residue in the soil complex. Such and other conclusions may be drawn, but, since the problem is now being investigated, we shall defer any further discussion.

There is, however, another point of interest in connection with the last experiment. This concerns the application of aluminum sulfate to suppress the alkalinity of solonetz soils. This has been tried by several workers (2), who found that the pH of the soil was temporarily lowered but climbed rather rapidly back to its original value. The original lowering of the pH is, of course, due to the sulfuric acid formed by hydrolysis. Some of the acid, however, remains in combination with the alumina even at high pH values. The later reversion of the pH is explained by the last equation. Some of the exchange-

able cations are displaced by Al, and the cation exchange capacity of the soil complex is permanently reduced. The acidic character of the complex has been weakened, its isoelectric point has been raised, and its power to bind bases is thereby partly suppressed. The method is obviously at fault.

THE SILICATED AND PHOSPHATED SOIL COMPLEX

If the OH ions in the basic residue of the amphoteric colloidal complex be displaced by the polyvalent anions of a weak acid which form a strongly associated compound with the basic group, there will result a new complex having a stronger acid residue, a weaker basic residue, a lower isoelectric point, and a higher cation exchange capacity.

Tables 135 and 136 show the effects of silicic and phosphoric acids upon the cation exchange capacity of the Sharkey, the Sassafras, and the Nipe soil colloids. Since the isoelectric point could not be determined in all cases, the colloids were all precipitated at the same pH. Although the strongly associat-

TABLE 135

The cation exchange capacity of the original and the silicated Sharkey, Sassafras, and Nipe soil colloids

Milliequivalents per gram

COLLOID	EXCHANGE CAPACITY		SiO_2 ADSORBED	INCREASE IN EXCHANGE CAPACITY	
	Original	Silicated			
	m.e.	*m.e.*	*mgm.*	*m.e.*	*per cent*
Sharkey	0.783	0.787	1.5	0.004	0.5
Sassafras	0.326	0.355	3.5	0.029	8.9
Nipe	0.126	0.247	18.5	0.121	96.0

ing anions will displace OH ions far above the isoelectric point of the colloids, the adsorption is greater at low pH where the OH ions in solution offer but little competition. Furthermore, a complete flocculation is obtained only near the isoelectric point. A pH of 3.2 was found suitable. This was far below the isoelectric point of the original Sassafras (about 4.3) and Nipe (about 6.0) and near that of the Sharkey.

The precipitation was carried out in the following manner:

One liter of a solution containing 7.5 millimols sodium silicate, for the silicate series, and 7.5 millimols disodium phosphate for the phosphate series, was rapidly mixed with 1 liter containing 1 gm. suspended colloid together with sufficient HCl to give a final pH of 3.2. The following day the clear, supernatant liquid was decanted, the precipitates were air dried, and the cation exchange capacity was determined as before stated. A second phosphate series was prepared with the same proportions but with a dilution of only one-tenth that of the first. This series is designated as the concentrated series.

The results show that the colloid with the highest isoelectric point, i.e., the

Nipe, adsorbs the greatest quantity of silicate and phosphate ions and exhibits the greatest increase in exchange capacity. The Sharkey colloid adsorbed so little SiO_2 and P_2O_5 from the dilute solutions that the small, yet fairly proportional, increases in the exchange capacities recorded must be looked upon as accidental results rather than as true values, since duplicate samples generally show greater differences.

In the concentrated series the Sharkey showed the highest increase in a proportionally higher phosphate adsorption whereas the increase in exchange capacity was small compared to that of the other colloids. We believe this difference to be real and to be due to a displacement of the silicate ion by the phosphate, which was proved by an analysis of the supernatant liquid.

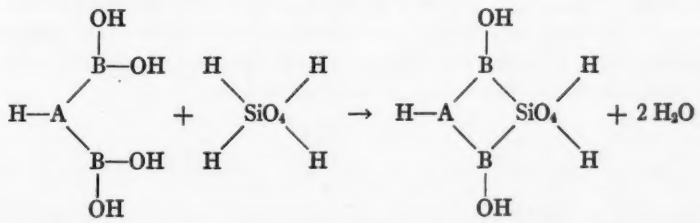
TABLE 136

The cation exchange capacity of the original and the phosphated Sharkey, Sassafras, and Nipe soil colloids

Milliequivalents per gram

COLLOID	EXCHANGE CAPACITY		P_2O_5 ADSORBED	INCREASE IN EXCHANGE CAPACITY	
	Original	Phosphated			
	m.e.	*m.e.*	*mgm.*	*m.e.*	*per cent*
Sharkey	0.783	0.789	1.0	0.006	0.8
Sassafras	0.326	0.399	2.9	0.073	22.4
Nipe	0.126	0.236	16.8	0.110	87.3
Concentrated series					
Sharkey		0.845	14.0	0.062	7.9
Sassafras		0.503	16.0	0.177	54.5
Nipe		0.332	18.0	0.206	165.0

The increase in the cation exchange capacity and the lowering of the isoelectric points may be illustrated by the equation:



This synthetic upbuild or regeneration of the soil complex must take place in the soil under certain favorable conditions. Thus the acidic complex in the A_2 horizon of a podzol will, at the cessation of the podzolizing conditions (the destruction of the raw humus covering), combine with and fix the weak bases previously kept mobile in the ionized condition. Through the weathering of the

minerals, through the action of burrowing animals, and through the decomposition of plant residue sufficient bases will finally be available for the synthetic regeneration of a more basic complex of the type met with in the brown soils. Such a complex will possess two advantages over the originally very acidic complex: (*a*) It will, by virtue of its stronger basic residue, more firmly fix the valuable PO_4 anion, and (*b*) it will require a smaller quantity of exchangeable cations (bases) to maintain a favorable pH.

The extremely basic complex in lateritic soils will, under certain conditions, combine with weak acids such as silicic and humic acids especially when these are present in a fairly acid soil solution. The complex thus built up would possess a stronger acid residue, the advantages of which would be: (*a*) a moderate power to bind cations, a power which is almost lacking in the laterites, and (*b*) a less firm fixation of the PO_4 anion, a fixation which is often too firm in the laterites.

The chances of a regeneration of the lateritic complex are probably more remote than in the case of the podzolic complex. The laterites are very deep, the source of silicic acid is largely exhausted, and humic acids do not long endure in lateritic regions. Nevertheless silicic acid is always pumped up by plants, and a certain change in the climate, drainage, and vegetation might very well lead to a regeneration of the lateritic soil complex.

SUMMARY

The amphoteric soil complex which represents partly hydrolyzed salts of polyvalent weak acids and bases is subject to the following destructive and constructive changes:

At low and at high pH the basic and the acidic groups, respectively, become ionized and are split off by hydrolytic cleavage and, since the ionized condition represents the most soluble, these groups may be permanently lost by the soil. This process leads to a degradation of the soil.

Under other conditions, favorable for the reaction, the degraded complex will unite with acidic or basic groups with which an isoelectric compound may be formed. Conditions permitting this synthetic upbuild will lead to a regeneration of the soil. A study of the aluminated, the silicated, and the phosphated soil colloids shows the conditions and nature of such reactions.

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